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<p>(21) International Application Number: PCT/US99/29947 (22) International Filing Date: 15 December 1999 (15.12.99)</p> <p>(30) Priority Data: 60/116,516 20 January 1999 (20.01.99) US</p> <p>(71) Applicant (<i>for all designated States except US</i>): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (<i>for US only</i>): KOTT, Kevin, Lee [US/US]; 2920 Bentbrook Drive, Cincinnati, OH 45251 (US). SCHEIBEL, Jeffrey, John [US/US]; 6651 Miami Trails Drive, Loveland, OH 45140 (US). SEVERSON, Roland, George [US/US]; 10184 Amberwood Court, Cincinnati, OH 45241 (US). CRIPE, Thomas, Anthony [US/US]; 599 Three Chimneys Lane, Loveland, OH 45140 (US). BURCKETT-ST. LAURENT, James, C., T., R. [GB/US]; 11477 Gideon Lane, Cincinnati, OH 45249 (US). WATSON, Randall, Alan [US/BE]; Snijdersdreef 3, B-3090 Overijse (BE). GARCIA, Raquel, Lopez [ES/ES]; San Pelayo 38, 4, E-36680 A Estrada (ES).</p>		<p>(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).</p> <p>(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: AQUEOUS HEAVY DUTY LIQUID DETERGENT COMPOSITIONS COMPRISING MODIFIED ALKYLBENZENE SULFONATES</p> <p>(57) Abstract</p> <p>The present invention relates to aqueous based heavy-duty liquid detergent compositions containing a modified alkylbenzene sulfonate surfactant (MABS), as co-surfactant (alkyl polyhydroxy fatty acid amide and/or alkyl amidopropyl dimethyl amine) and an aqueous liquid carrier. The MABS comprises a mixture of specific branched and non-branched alkylbenzene sulfonate compounds, which are further characterised by a 2/3-phenyl index of 160-275.</p>			

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AQUEOUS HEAVY DUTY LIQUID DETERGENT COMPOSITIONS COMPRISING MODIFIED
ALKYLBENZENE SULFONATES

FIELD OF THE INVENTION

This invention relates to heavy duty liquid laundry detergent products which are aqueous in nature and which include particular types of improved alkylbenzene sulfonate surfactant mixtures adapted for use by controlling compositional parameters, especially a 2/3-phenyl index and a 2-methyl-2-phenyl index.

BACKGROUND OF THE INVENTION

Historically, highly branched alkylbenzene sulfonate surfactants, such as those based on tetrapropylene, known as "ABS" or "TPBS", were used in detergents. However, these were found to be very poorly biodegradable. A long period followed of improving manufacturing processes for alkylbenzene sulfonates, making them as linear as practically possible, hence the acronym "LAS". The overwhelming part of a large art of linear alkylbenzene sulfonate surfactant manufacture is directed to this objective. All relevant large-scale commercial alkylbenzene sulfonate processes in use today are directed to linear alkylbenzene sulfonates. However, linear alkylbenzene sulfonates are not without limitations; for example, they would be more desirable if improved for hard water cleaning and/or cold water cleaning properties. They can often fail to produce good cleaning results, for example when used in hard water areas.

As a result of the limitations of the alkylbenzene sulfonates, consumer cleaning formulations have often needed to include a higher level of cosurfactants, builders, and other additives than would have been needed given a superior alkylbenzene sulfonate.

The art of alkylbenzene sulfonate detergents is replete with references which teach both for and against almost every aspect of these compositions. Moreover, there are believed to be erroneous teachings and technical misconceptions about the mechanism of LAS operation under in-use conditions, particularly in the area of hardness tolerance. The volume of such references debases the art as a whole and makes it difficult to select the useful teachings from the useless without repeated experimentation. To further

understand the state of the art, it should be appreciated that there has been not only a lack of clarity on which way to go to fix the unresolved problems of linear LAS, but also a range of misconceptions, not only in the understanding of biodegradation but also in basic mechanisms of operation of LAS in presence of hardness.

Also, while the currently commercial, essentially linear alkylbenzene sulfonate surfactants are relatively simple compositions to define and analyze, compositions containing both branched and linear alkylbenzene sulfonate surfactants are complex. In general such compositions can be highly varied, containing one or more different kinds of branching in any of a number of positions on the aliphatic chain. A very large number, e.g., hundreds, of distinct chemical species are possible in such mixtures. Accordingly there is an onerous burden of experimentation if it is desired to improve such compositions so that they can clean better in detergent compositions while at the same time remaining biodegradable. The formulator's knowledge is key to guiding this effort.

Yet another currently unresolved problem in alkylbenzene sulfonate manufacture is to make more effective use of current LAB feedstocks. It would be highly desirable, both from a performance point of view and from an economic point of view, to better utilize certain desirable types of branched hydrocarbons.

Accordingly there is a substantial unmet need for further improvements in alkylbenzene sulfonate surfactant mixtures, especially with respect to those offering one or more of the advantages of superior cleaning, hardness tolerance, satisfactory biodegradability, and cost.

BACKGROUND ART

US 5,659,099; US 5,393,718; US 5,256,392; US 5,227,558; US 5,139,759; US 5,164,169; US 5,116,794; US 4,840,929; US 5,744,673; US 5,522,984; US 5,811,623; US 5,777,187; WO 9,729,064; WO 9,747,573; WO 9,729,063; US 5,026,933; US 4,990,718; US 4,301,316; US 4,301,317; US 4,855,527; US 4,870,038; US 2,477,382; EP 466,558; 1/15/92; EP 469,940; 2/5/92; FR 2,697,246; 4/29/94; SU 793,972; 1/7/81; US 2,564,072; US 3,196,174; US 3,238,249; US 3,355,484; US 3,442,964; US 3,492,364; US 4,959,491; WO 88/07030; 9/25/90; US 4,962,256; US 5,196,624; US 5,196,625; EP 364,012 B; 2/15/90; US 3,312,745; US 3,341,614; US 3,442,965; US 3,674,885; US 4,447,664; US 4,533,651; US 4,587,374; US 4,996,386; US 5,210,060;

US 5,510,306; WO 95/17961, 7/6/95; WO 95/18084; US 5,510,306; US 5,087,788; US 4,301,316; US 4,301,317; US 4,855,527; US 4,870,038; US 5,026,933; US 5,625,105 and US 4,973,788. See Vol 56 in "Surfactant Science" series, Marcel Dekker, New York, 1996, including in particular Chapter 2 entitled "Alkylarylsulfonates: History, Manufacture, Analysis and Environmental Properties", pages 39-108, "Surfactant Science" series, Vol 73, Marcel Dekker, New York, 1998 and "Surfactant Science" series, Vol 40, Marcel Dekker, New York, 1992. See also copending U.S. Patent applications No. 60/053,319 Attorney docket No 6766P filed on July 21st, 1997, No. 60/053,318, Attorney docket No 6767P filed on July 21st, 1997, No. 60/053,321, Attorney docket No 6768P filed on July 21st, 1997, No. 60/053,209, Attorney docket No 6769P filed on July 21st, 1997, No. 60/053,328, Attorney docket No 6770P filed on July 21st, 1997, No. 60/053,186, Attorney docket No 6771P filed on July 21st, 1997 and the art cited therein. Documents referenced herein are incorporated in their entirety.

SUMMARY OF THE INVENTION

The present invention provides aqueous heavy-duty liquid detergent compositions comprising modified alkylbenzene sulfonate surfactant mixtures.

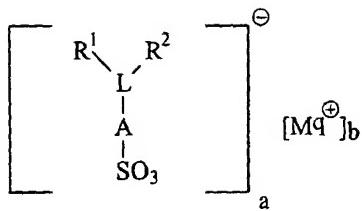
Specifically, the present invention comprises an aqueous heavy-duty liquid detergent composition.

The aqueous based heavy duty laundry detergent compositions herein preferably contain a surfactant system comprising surfactants selected from nonionic detergents, anionic detergents, zwitterionic detergents, amine oxide detergents, and mixtures thereof.

Specifically, the first embodiment of the present invention comprises an aqueous based heavy duty laundry detergent composition comprising:

(i) from about 5% to about 70% by weight of composition of a modified alkylbenzene sulfonate surfactant mixture comprising:

(a) from about 15% to about 99% by weight of surfactant mixture, a mixture of branched alkylbenzene sulfonates having formula (I):

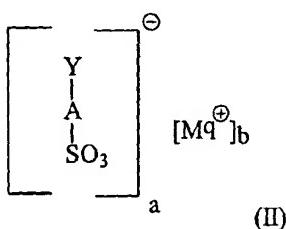


(I)

wherein L is an acyclic aliphatic moiety consisting of carbon and hydrogen, said L having two methyl termini and said L having no substituents other than A, R¹ and R²; and wherein said mixture of branched alkylbenzene sulfonates contains two or more of said branched alkylbenzene sulfonates differing in molecular weight of the anion of said formula (I) and wherein said mixture of branched alkylbenzene sulfonates has

- a sum of carbon atoms in R¹, L and R² of from 9 to 15;
- an average aliphatic carbon content of from about 10.0 to about 14.0 carbon atoms; M is a cation or cation mixture having a valence q; a and b are integers selected such that said branched alkylbenzene sulfonates are electroneutral; R¹ is C₁-C₃ alkyl; R² is selected from H and C₁-C₃ alkyl; A is a benzene moiety; and

(b) from about 1% to about 85% by weight of surfactant mixture, of a mixture of nonbranched alkylbenzene sulfonates having formula (II):



wherein a, b, M, A and q are as defined hereinbefore and Y is an unsubstituted linear aliphatic moiety consisting of carbon and hydrogen having two methyl termini, and wherein said Y has a sum of carbon atoms of from 9 to 15, preferably from 10 to 14, and said Y has an average aliphatic carbon content of from about 10.0 to about 14.0; and

wherein said modified alkylbenzene sulfonate surfactant mixture is further characterized by a 2/3-phenyl index of from about 160 to about 275;

- (ii) from about 0.1 to about 8% of a co-surfactant composition selected from the group consisting of alkyl polyhydroxy fatty acid amide, alkyl amidopropyl dimethyl amine and mixtures thereof; and

- (iii) from about 30% to about 95%, of an aqueous liquid carrier;

wherein said composition is further characterized by a 2/3-phenyl index of from about 160 to about 275.

Specifically, the second embodiment of the present invention comprises an aqueous based heavy duty laundry detergent composition comprising:

- (i) a modified alkylbenzene sulfonate surfactant mixture comprising the product of a process comprising the steps of:

- (I) alkylating benzene with an alkylating mixture in the presence of a zeolite beta catalyst;
- (II) sulfonating the product of (I); and
- (III) neutralizing the product of (II);

wherein said alkylating mixture comprises:

- (a) from about 1% to about 99.9%, by weight of alkylating mixture of branched C₉-C₂₀ monoolefins, said branched monoolefins having structures identical with those of the branched monoolefins formed by dehydrogenating branched paraffins of formula R¹LR² wherein L is an acyclic aliphatic moiety consisting of carbon and hydrogen and containing two terminal methyls; R¹ is C₁ to C₃ alkyl; and R² is selected from H and C₁ to C₃ alkyl; and

- (b) from about 0.1% to about 85%, by weight of alkylating mixture of C₉-C₂₀ linear aliphatic olefins;

wherein said alkylating mixture contains said branched C₉-C₂₀ monoolefins having at least two different carbon numbers in said C₉-C₂₀ range, and has a mean carbon content of from about 9.0 to about 15.0 carbon atoms; and wherein said components (a) and (b) are at a weight ratio of at least about 15:85;

(ii) from about 0.1 to about 8% of a co-surfactant composition selected from the group consisting of alkyl polyhydroxy fatty acid amide, alkyl amidopropyl dimethyl amine and mixtures thereof; and
(iii) from about 30% to about 95%, of an aqueous liquid carrier;
wherein said composition is further characterized by a 2/3-phenyl index of from about 160 to about 275.

Specifically, the third embodiment of the present invention comprises an aqueous based heavy duty laundry detergent composition comprising:

(i) a modified alkylbenzene sulfonate surfactant mixture consisting essentially of the product of a process comprising the steps, in sequence, of:

- (I) alkylating benzene with an alkylating mixture in the presence of a zeolite beta catalyst;
- (II) sulfonating the product of (I); and
- (III) neutralizing the product of (II);

wherein said alkylating mixture comprises:

(a) from about 1% to about 99.9%, by weight of alkylating mixture of a branched alkylating agent selected from the group consisting of:

(A) C₉-C₂₀ internal monoolefins R¹LR² wherein L is an acyclic olefinic moiety consisting of carbon and hydrogen and containing two terminal methyls;

(B) C₉-C₂₀ alpha monoolefins R¹AR² wherein A is an acyclic alpha-olefinic moiety consisting of carbon and hydrogen and containing one terminal methyl and one terminal olefinic methylene;

(C) C₉-C₂₀ vinylidene monoolefins R¹BR² wherein B is an acyclic vinylidene olefin moiety consisting of carbon and hydrogen and containing two terminal methyls and one internal olefinic methylene;

(D) C₉-C₂₀ primary alcohols R¹QR² wherein Q is an acyclic aliphatic primary terminal alcohol moiety consisting of carbon, hydrogen and oxygen and containing one terminal methyl;

(E) C₉-C₂₀ primary alcohols R¹ZR² wherein Z is an acyclic aliphatic primary nonterminal alcohol moiety consisting of carbon, hydrogen and oxygen and containing two terminal methyls; and

(F) mixtures thereof;

wherein in any of (A)-(F), said R¹ is C₁ to C₃ alkyl and said R² is selected from H and C₁ to C₃ alkyl; and

(b) from about 0.1% to about 85%, by weight of alkylating mixture of C₉-C₂₀ linear alkylating agent selected from C₉-C₂₀ linear aliphatic olefins, C₉-C₂₀ linear aliphatic alcohols and mixtures thereof;

wherein said alkylating mixture contains said branched alkylating agents having at least two different carbon numbers in said C₉-C₂₀ range, and has a mean carbon content of from about 9.0 to about 15.0 carbon atoms; and wherein said components (a) and (b) are at a weight ratio of at least about 15:85;

(ii) from about 0.1 to about 8% of a co-surfactant composition selected from the group consisting of alkyl polyhydroxy fatty acid amide, alkyl amidopropyl dimethyl amine and mixtures thereof; and

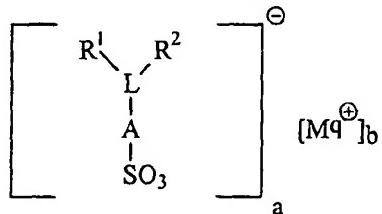
(iii) from about 30% to about 95%, of an aqueous liquid carrier;

wherein said composition is further characterized by a 2/3-phenyl index of from about 160 to about 275.

Specifically, the fourth embodiment of the present invention comprises an aqueous based heavy duty laundry detergent composition comprising:

(i) from about 5% to about 70% by weight of composition of a modified alkylbenzene sulfonate surfactant mixture comprising:

(a) from about 15% to about 99% by weight of surfactant mixture, a mixture of branched alkylbenzene sulfonates having formula (I):

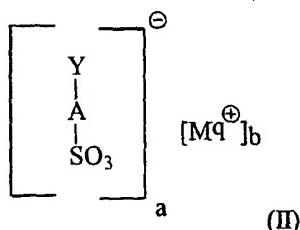


(I)

wherein L is an acyclic aliphatic moiety consisting of carbon and hydrogen, said L having two methyl termini and said L having no substituents other than A, R¹ and R²; and wherein said mixture of branched alkylbenzene sulfonates contains two or more of said branched alkylbenzene sulfonates differing in molecular weight of the anion of said formula (I) and wherein said mixture of branched alkylbenzene sulfonates has

- a sum of carbon atoms in R¹, L and R² of from 9 to 15;
- an average aliphatic carbon content of from about 10.0 to about 14.0 carbon atoms; M is a cation or cation mixture having a valence q; a and b are integers selected such that said branched alkylbenzene sulfonates are electroneutral; R¹ is C₁-C₃ alkyl; R² is selected from H and C₁-C₃ alkyl; A is a benzene moiety; and

(b) from about 1% to about 85% by weight of surfactant mixture, of a mixture of nonbranched alkylbenzene sulfonates having formula (II):



wherein a, b, M, A and q are as defined hereinbefore and Y is an unsubstituted linear aliphatic moiety consisting of carbon and hydrogen having two methyl termini, and wherein said Y has a sum of carbon atoms of from 9 to 15, preferably from 10 to 14, and said Y has an average aliphatic carbon content of from about 10.0 to about 14.0; and

wherein said modified alkylbenzene sulfonate surfactant mixture is further characterized by a 2/3-phenyl index of from about 160 to about 275 and wherein said modified alkylbenzene sulfonate surfactant mixture has a 2-methyl-2-phenyl index of less than about 0.3;

- (ii) from about 0.1 to about 8% of a co-surfactant composition selected from the group consisting of alkyl polyhydroxy fatty acid amide, alkyl amidopropyl dimethyl amine and mixtures thereof;
- (iii) from about 0.00001% to about 99.9% of composition of a surfactant selected from the group consisting of anionic surfactants other than those of (i), nonionic surfactants, zwitterionic surfactants, cationic surfactants, amphoteric surfactant and mixtures thereof; and
- (iv) from about 30% to about 95%, of an aqueous liquid carrier;

provided that when said detergent composition comprises any alkylbenzene sulfonate surfactant other than said modified alkylbenzene sulfonate surfactant mixture, said detergent composition is further characterized by an overall 2/3-phenyl index of at least about 160, wherein said overall 2/3-phenyl index is determined by measuring 2/3-phenyl index, as defined herein, on a blend of said modified alkylbenzene sulfonate surfactant mixture and said any other alkylbenzene sulfonate to be added to said detergent composition, said blend, for purposes of measurement, being prepared from aliquots of said modified alkylbenzene sulfonate surfactant mixture and said other alkylbenzene sulfonate not yet exposed to any other of said components of the detergent composition; and further provided that when said detergent composition comprises any alkylbenzene sulfonate surfactant other than said modified alkylbenzene sulfonate surfactant mixture, said detergent composition is further characterized by an overall 2-methyl-2-phenyl index of less than about 0.3, wherein said overall 2-methyl-2-phenyl index is to be determined by measuring 2-methyl-2-phenyl index, as defined herein, on a blend of said modified alkylbenzene sulfonate surfactant mixture and any other alkylbenzene sulfonate to be added to said detergent composition, said blend, for purposes of measurement, being prepared from aliquots of said modified alkylbenzene sulfonate surfactant mixture and said other alkylbenzene sulfonate not yet exposed to any other of said components of the detergent composition.

The detergent compositions defined herein also comprise from about 1% to 80% by weight of the composition of additional detergent ingredients such as builders, enzymes, colorants, bleaching agents, bleach activators, colored speckles, organic detergent builders, inorganic alkalinity sources and mixtures thereof.

The above mentioned embodiments and other aspects of the present invention are more fully described and exemplified in the detailed description hereinafter.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius ($^{\circ}\text{C}$) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The aqueous liquid detergent compositions of this invention comprise a modified alkylbenzene sulfonate surfactant mixture. The essential and optional components of the modified alkylbenzene sulfonate surfactant mixture and other optional materials of the aqueous liquid detergent compositions herein, as well as composition form, preparation and use, are described in greater detail as follows: (All concentrations and ratios are on a weight basis unless otherwise specified.) The invention, on the other hand, is not intended to encompass any wholly conventional liquid detergent compositions, such as those based exclusively on linear alkylbenzene sulfonates made by any process, or exclusively on known unacceptably branched alkylbenzene sulfonates such as ABS or TPBS.

It is preferred that when the detergent compositions of the present invention comprise any alkylbenzene sulfonate surfactant other than said modified alkylbenzene sulfonate surfactant mixture (for example as a result of blending into the detergent composition one or more commercial, especially linear, typically linear C₁₀-C₁₄, alkylbenzene sulfonate surfactants), said composition is further characterized by an overall 2/3-phenyl index of at least about 200, preferably at least about 250, more preferably at least about 350, more preferably still, at least about 500, wherein said overall 2/3-phenyl index is determined by measuring 2/3-phenyl index, as defined herein, on a blend of said modified alkylbenzene sulfonate surfactant mixture and said any other alkylbenzene sulfonate to be added to said composition, said blend, for purposes of measurement, being prepared from aliquots of said modified alkylbenzene sulfonate surfactant mixture and said other alkylbenzene sulfonate not yet exposed to any other of the components of said composition; and further provided that when said composition comprises any alkylbenzene sulfonate surfactant other than said modified alkylbenzene sulfonate surfactant mixture (for example as a result of blending into the composition one

or more commercial, especially linear, typically linear C₁₀-C₁₄, alkylbenzene sulfonate surfactants), said composition is further characterized by an overall 2-methyl-2-phenyl index of less than about 0.3, preferably from 0 to 0.2, more preferably no more than about 0.1, more preferably still, no more than about 0.05, wherein said overall 2-methyl-2-phenyl index is to be determined by measuring 2-methyl-2-phenyl index, as defined herein, on a blend of said modified alkylbenzene sulfonate surfactant mixture and any other alkylbenzene sulfonate to be added to said composition, said blend, for purposes of measurement, being prepared from aliquots of said modified alkylbenzene sulfonate surfactant mixture and said other alkylbenzene sulfonate not yet exposed to any other of the components of said composition. These provisions may appear somewhat unusual, however they are consistent with the spirit and scope of the present invention, which encompasses a number of economical but less preferred approaches in terms of overall cleaning performance, such as blending of the modified alkylbenzene sulfonate surfactants with conventional linear alkylbenzene sulfonate surfactants either during synthesis or during formulation into the composition. Moreover, as is well known to practitioners of hand dishwashing analysis, a number of hand dishwashing adjuncts (paramagnetic materials and sometimes even water) are capable of interfering with methods for determining the parameters of alkylbenzene sulfonate surfactant mixtures as described hereinafter. Hence wherever possible, analysis should be conducted on dry materials before mixing them into the compositions.

In one preferred embodiment the modified alkylbenzene sulfonate surfactant mixture in the hand dishwashing composition according to the composition according to the first embodiment is prepared by a process comprising a step selected from:

blending a mixture of branched and linear alkylbenzene sulfonate surfactants having a 2/3-phenyl index of 500 to 700 with an alkylbenzene sulfonate surfactant mixture having a 2/3-phenyl index of 75 to 160 (typically this alkylbenzene sulfonate surfactant is a commercial C₁₀-C₁₄ linear alkylbenzene sulfonate surfactant, e.g., DETAL ® process LAS or HF process LAS though in general any commercial linear (LAS) or branched (ABS, TPBS) type can be used); and

blending a mixture of branched and linear alkylbenzenes having a 2/3-phenyl index of 500 to 700 with an alkylbenzene mixture having a 2/3-phenyl index of 75 to 160 and sulfonating said blend.

Moreover, the invention encompasses the addition of useful hydrotrope precursors and/or hydrotropes, such as C₁-C₈ alkylbenzenes, more typically toluenes, cumenes, xylenes, naphthalenes, or the sulfonated derivatives of any such materials, minor amounts of any other materials, such as tribranched alkylbenzene sulfonate surfactants, dialkylbenzenes and their derivatives, dialkyl tetralins, wetting agents, processing aids, and the like. It will be understood that, with the exception of hydrotropes, it will not be usual practice in the present invention to include any such materials. Likewise it will be understood that such materials, if and when they interfere with analytical methods, will not be included in samples of compositions used for analytical purposes.

A preferred modified alkylbenzene sulfonate surfactant mixture according to first embodiment of the present invention has M selected from H, Na, K and mixtures thereof, said a=1, said b=1, said q=1, and said modified alkylbenzene sulfonate surfactant mixture has a 2-methyl-2-phenyl index of less than about 0.3, preferably less than about 0.2, more preferably from 0 to about 0.1.

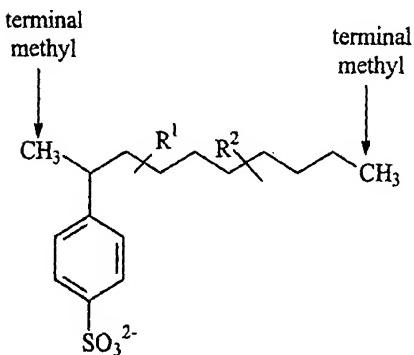
Related to the composition are methods of their use, such as a method contacting soiled tableware in need of cleaning with either a neat or an aqueous solution of the composition of the invention. Such methods may optionally include the step of diluting the composition with water. Furthermore, the composition may be applied, either neat or as an aqueous solution, directly to the tableware or surface to be cleaned or directly to a cleaning implement, such as a sponge or a wash cloth. Such methods are part of the present invention.

Such a modified alkylbenzene sulfonate surfactant mixture according can be made as the product of a process using as catalyst a zeolite selected from mordenite, offretite and H-ZSM-12 in at least partially acidic form, preferably an acidic mordenite (in general certain forms of zeolite beta can be used as an alternative but are not preferred). Embodiments described in terms of their making, as well as suitable catalysts, are all further detailed hereinafter.

Another preferred modified alkylbenzene sulfonate surfactant mixture according to the first embodiment of the invention consists essentially of said mixture of branched alkylbenzene sulfonates and nonbranched alkylbenzene sulfonates, wherein said 2-methyl-2-phenyl index of said modified alkylbenzene sulfonate surfactant mixture is less than about 0.1, and wherein in said mixture of branched and nonbranched alkylbenzene sulfonates, said average aliphatic carbon content is from about 11.5 to about 12.5 carbon atoms; said R¹ is methyl; said R² is selected from H and methyl provided that in at least about 0.7 mole fraction of said branched alkylbenzene sulfonates R² is H; and wherein said sum of carbon atoms in R¹, L and R² is from 10 to 14; and further wherein in said mixture of nonbranched alkylbenzene sulfonates, said Y has a sum of carbon atoms of from 10 to 14 carbon atoms, said average aliphatic carbon content of said nonbranched alkylbenzene sulfonates is from about 11.5 to about 12.5 carbon atoms, and said M is a monovalent cation or cation mixture selected from H, Na and mixtures thereof.

Definitions:

Methyl termini The terms "methyl termini" and/or "terminal methyl" mean the carbon atoms which are the terminal carbon atoms in alkyl moieties, that is L, and/or Y of formula (I) and formula (II) respectively are always bonded to three hydrogen atoms. That is, they will form a CH₃- group. To better explain this, the structure below shows the two terminal methyl groups in an alkylbenzene sulfonate.



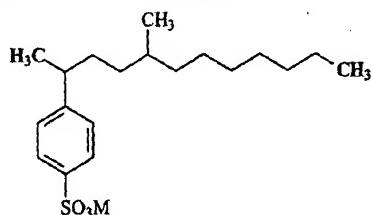
The term "AB" herein when used without further qualification is an abbreviation for "alkylbenzene" of the so-called "hard" or nonbiodegradable type which on sulfonation forms "ABS". The term "LAB" herein is an abbreviation for "linear alkylbenzene" of the

current commercial, more biodegradable type, which on sulfonation forms linear alkylbenzene sulfonate, or "LAS". The term "MLAS" herein is an abbreviation for the modified alkylbenzene sulfonate mixtures of the invention.

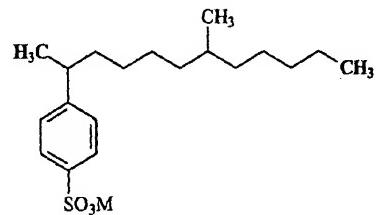
Impurities: The surfactant mixtures herein are preferably substantially free from impurities selected from tribranched impurities, dialkyl tetralin impurities and mixtures thereof. By "substantially free" it is meant that the amounts of such impurities are insufficient to contribute positively or negatively to the cleaning effectiveness of the composition. Typically there is less than about 5%, preferably less than about 1%, more preferably about 0.1% or less of the impurity, that is typically no one of the impurities is practically detectable.

Illustrative Structures

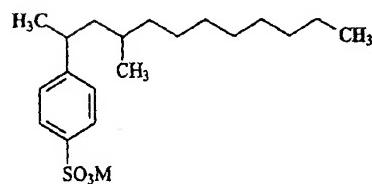
The better to illustrate the possible complexity of modified alkylbenzene sulfonate surfactant mixtures of the invention and the resulting detergent compositions, structures (a) to (v) below are illustrative of some of the many preferred compounds of formula (I). These are only a few of hundreds of possible preferred structures that make up the bulk of the composition, and should not be taken as limiting of the invention.



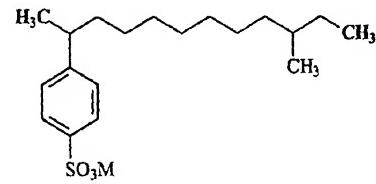
(a)



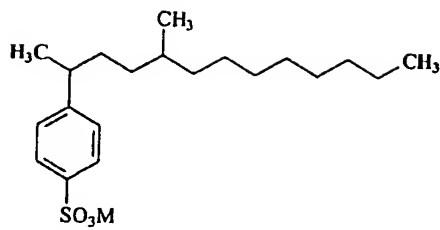
(b)



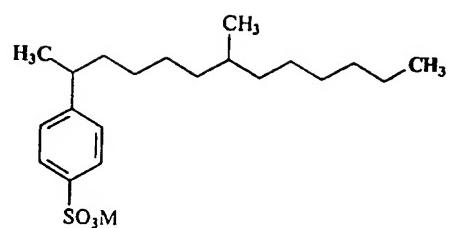
(c)



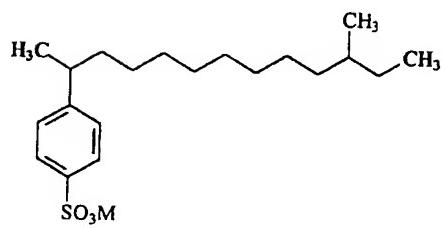
(d)



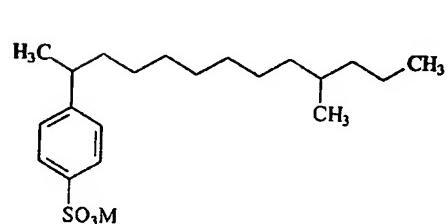
(e)



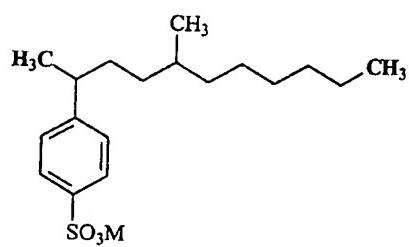
(f)



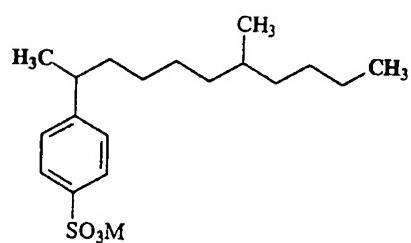
(g)



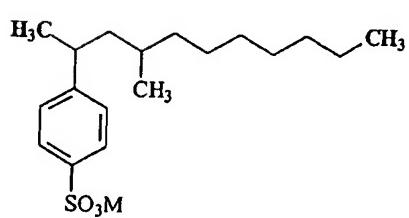
(h)



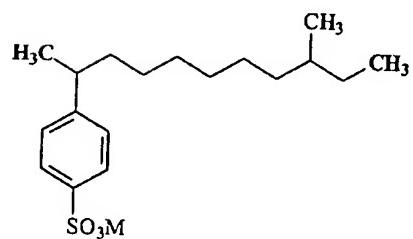
(i)



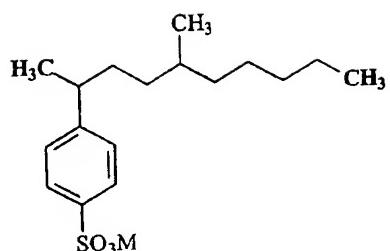
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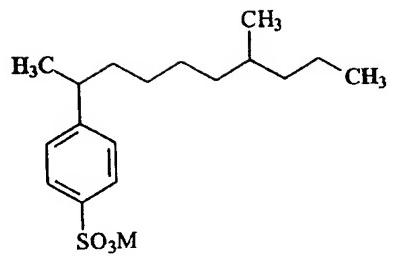
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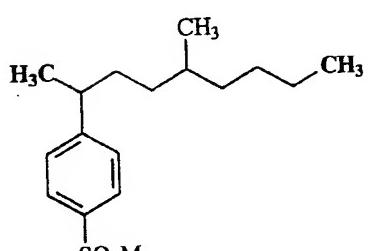
(l)



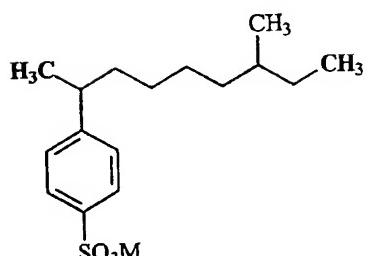
(m)



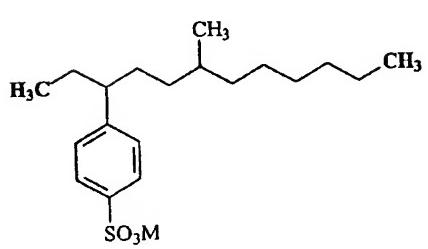
(n)



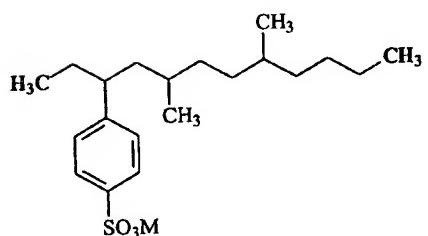
(o)



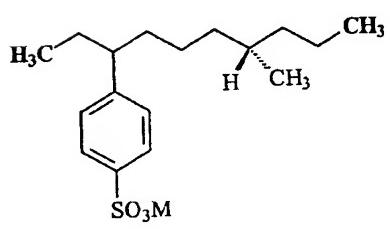
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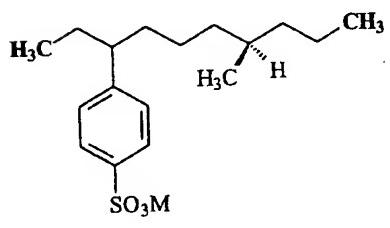
(q)



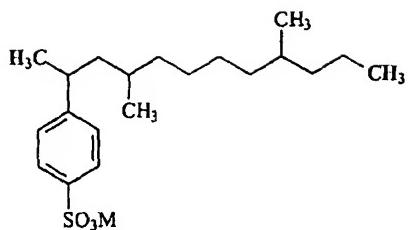
(r)



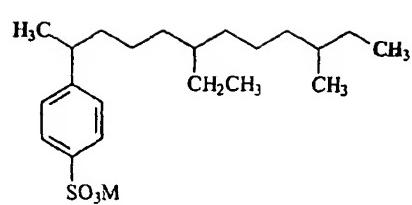
(s)



(t)

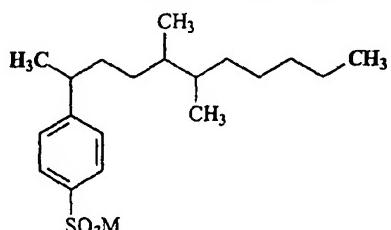


(u)

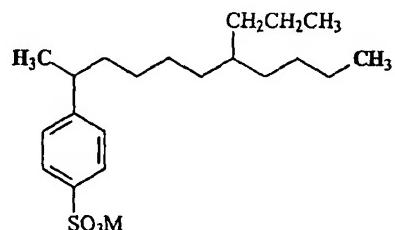


(v)

Structures (w) and (x) nonlimitingly illustrate less preferred compounds of Formula (I) which can be present, at lower levels than the above-illustrated preferred types of structures, in the modified alkylbenzene sulfonate surfactant mixtures of the invention and the resulting detergent compositions.

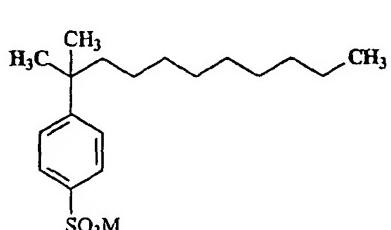


(w)

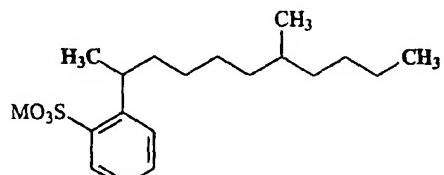


(x)

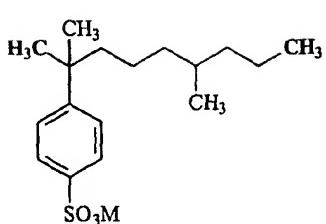
Structures (y), (z), and (aa) nonlimitingly illustrate compounds broadly within Formula (I) that are not preferred but which can be present in the modified alkylbenzene sulfonate surfactant mixtures of the invention and the resulting detergent compositions.



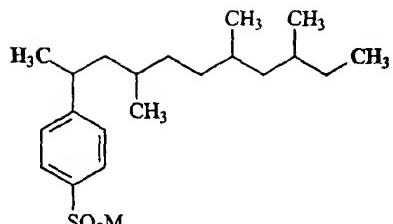
(y)



(z)



(aa)



(bb)

Structure (bb) is illustrative of a tri-branched structure not within Formula (I), but that can be present as an impurity.

Preferably the branched alkylbenzene sulfonate is the product of sulfonating a branched alkylbenzene, wherein the branched alkylbenzene is produced by alkylating benzene with a branched olefin over an zeolite beta catalyst which may be fluoridated or non-fluoridated, more preferably the zeolite beta catalyst is an acidic zeolite beta catalyst. The preferred acidic zeolite beta catalysts are HF-treated calcined zeolite beta catalysts.

In outline, modified alkylbenzene sulfonate surfactant mixtures herein can be made by the steps of:

- (I) alkylating benzene with an alkylating mixture;
- (II) sulfonating the product of (I); and (optionally but very preferably)
- (III) neutralizing the product of (II).

Provided that suitable alkylation catalysts and process conditions as taught herein are used, the product of step (I) is a modified alkylbenzene mixture in accordance with the invention. Provided that sulfonation is conducted under conditions generally known and reapplicable from LAS manufacture, see for example the literature references cited herein, the product of step (II) is a modified alkylbenzene sulfonic acid mixture in accordance with the invention. Provided that neutralization step (III) is conducted as generally taught herein, the product of step (III) is a modified alkylbenzene sulfonate surfactant mixture in accordance with the invention. Since neutralization can be incomplete, mixtures of the acid and neutralized forms of the present modified alkylbenzene sulfonate systems in all proportions, e.g., from about 1000:1 to 1:1000 by weight, are also part of the present invention. Overall, the greatest criticalities are in step (I).

Thus it is further preferred that in step (I) the alkylation is performed at a temperature of from about 125°C to about 230°C, preferably from about 175°C to about 215°C and at a pressure of from about 50 psig to about 1000 psig, preferably from about 100 psig to about 250 psig. Time for this alkylation reaction can vary, however it is further preferred that the time for this alkylation be from about 0.01 hour to about 18 hours, more preferably, as rapidly as possible, more typically from about 0.1 hour to about 5 hours, or from about 0.1 hour to about 3 hours.

In general it is found preferable in step (I) to couple together the use of relatively low temperatures (e.g., 175°C to about 215°C) with reaction times of medium duration (1 hour to about 8 hours) in the above-indicated ranges.

Moreover, it is contemplated that the alkylation "step" (I) herein can be "staged" so that two or more reactors operating under different conditions in the defined ranges may be useful. By operating a plurality of such reactors, it is possible to allow for material with less preferred 2-methyl-2-phenyl index to be initially formed and, surprisingly, to convert such material into material with a more preferred 2-methyl-2-phenyl index.

Thus a surprising discovery as part of the present invention is that one can attain low levels of quaternary alkylbenzenes in zeolite beta catalyzed reactions of benzene with branched olefins, as characterized by a 2-methyl-2-phenyl index of less than 0.1.

Alkylation Catalyst

The present invention uses a particularly defined alkylation catalyst. Such catalyst comprises a moderate acidity, medium-pore zeolite defined in detail hereinafter. A particularly preferred alkylation catalyst comprises at least partially dealuminized acidic nonfluoridated or at least partially dealuminized acidic fluoridated zeolite beta.

Numerous alkylation catalysts are readily determined to be unsuitable. Unsuitable alkylation catalysts include the DETAL® process catalysts, aluminum chloride, HF, and many others. Indeed no alkylation catalyst currently used for alkylation in the commercial production of detergent linear alkylbenzenesulfonates is suitable.

In contrast, suitable alkylation catalyst herein is selected from shape-selective moderately acidic alkylation catalysts, preferably zeolitic. More particularly, the zeolite in such catalysts for the alkylation step I is preferably selected from the group

consisting of ZSM-4, ZSM-20, and zeolite beta, more preferably zeolite beta, in at least partially acidic form. More preferably, the zeolite in step I (the alkylation step) is substantially in acid form and is contained in a catalyst pellet comprising a conventional binder and further wherein said catalyst pellet comprises at least about 1 %, more preferably at least 5%, more typically from 50% to about 90%, of said zeolite, wherein said zeolite is preferably a zeolite beta. More generally, suitable alkylation catalyst is typically at least partially crystalline, more preferably substantially crystalline not including binders or other materials used to form catalyst pellets, aggregates or composites. Moreover the catalyst is typically at least partially acidic zeolite beta. This catalyst is useful for the alkylation step identified as step I in the claims hereinafter.

The largest pore diameter characterizing the zeolites useful in the present alkylation process may be in the range of 6Angstrom to 8Angstrom, such as in zeolite beta. It should be understood that, in any case, the zeolites used as catalysts in the alkylation step of the present process have a major pore dimension intermediate between that of the large pore zeolites, such as the X and Y zeolites, and the relatively smaller pore size zeolites such as mordenite, offretite, HZSM-12 and HZSM-5. Indeed ZSM-5 has been tried and found inoperable in the present invention. The pore size dimensions and crystal structures of certain zeolites are specified in ATLAS OF ZEOLITE STRUCTURE TYPES by W. M. Meier and D. H. Olson, published by the Structure Commission of the International Zeolite Association (1978 and more recent editions) and distributed by Polycrystal Book Service, Pittsburgh, Pa.

The zeolites useful in the alkylation step of the instant process generally have at least 10 percent of the cationic sites thereof occupied by ions other than alkali or alkaline-earth metals. Typical but non-limiting replacing ions include ammonium, hydrogen, rare earth, zinc, copper and aluminum. Of this group, particular preference is accorded ammonium, hydrogen, rare earth or combinations thereof. In a preferred embodiment, the zeolites are converted to the predominantly hydrogen form, generally by replacement of the alkali metal or other ion originally present with hydrogen ion precursors, e.g., ammonium ions, which upon calcination yield the hydrogen form. This exchange is conveniently carried out by contact of the zeolite with an ammonium salt solution, e.g., ammonium chloride, utilizing well known ion exchange techniques. In

certain preferred embodiments, the extent of replacement is such as to produce a zeolite material in which at least 50 percent of the cationic sites are occupied by hydrogen ions.

The zeolites may be subjected to various chemical treatments, including alumina extraction (dealumination) and combination with one or more metal components, particularly the metals of Groups IIIB, III, IV, VI, VII and VIII. It is also contemplated that the zeolites may, in some instances, desirably be subjected to thermal treatment, including steaming or calcination in air, hydrogen or an inert gas, e.g. nitrogen or helium.

A suitable modifying treatment entails steaming of the zeolite by contact with an atmosphere containing from about 5 to about 100% steam at a temperature of from about 250°C to 1000°C. Steaming may last for a period of between about 0.25 and about 100 hours and may be conducted at pressures ranging from sub-atmospheric to several hundred atmospheres.

In practicing the desired alkylation step of the instant process, it may be useful to incorporate the above-described intermediate pore size crystalline zeolites in another material, e.g., a binder or matrix resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica, and/or metal oxides. Matrix materials can be in the form of gels including mixtures of silica and metal oxides. The latter may be either naturally occurring or in the form of gels or gelatinous precipitates. Naturally occurring clays which can be composited with the zeolite include those of the montmorillonite and kaolin families, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee-Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the intermediate pore size zeolites employed herein may be compounded with a porous matrix material, such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, and silica-titania, as well as ternary combinations, such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix may be in the form of a cogel. The relative proportions of finely divided zeolite and inorganic oxide gel

matrix may vary widely, with the zeolite content ranging from between about 1 to about 99% by weight and more usually in the range of about 5 to about 80% by weight of the composite.

A group of zeolites which includes some useful for the alkylation step herein have a silica:alumina ratio of at least 10:1, preferably at least 20:1. The silica:alumina ratios referred to in this specification are the structural or framework ratios, that is, the ratio for the SiO_4 to the AlO_4 tetrahedra. This ratio may vary from the silica:alumina ratio determined by various physical and chemical methods. For example, a gross chemical analysis may include aluminum which is present in the form of cations associated with the acidic sites on the zeolite, thereby giving a low silica:alumina ratio. Similarly, if the ratio is determined by thermogravimetric analysis (TGA) of ammonia desorption, a low ammonia titration may be obtained if cationic aluminum prevents exchange of the ammonium ions onto the acidic sites. These disparities are particularly troublesome when certain treatments such as the dealuminization methods described below which result in the presence of ionic aluminum free of the zeolite structure are employed. Due care should therefore be taken to ensure that the framework silica:alumina ratio is correctly determined.

When the zeolites have been prepared in the presence of organic cations they are catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solution. They may be activated by heating in an inert atmosphere at 540°C. for one hour, for example, followed by base exchange with ammonium salts followed by calcination at 540°C in air. The presence of organic cations in the forming solution may not be absolutely essential to the formation of the zeolite; but it does appear to favor the formation of this special type of zeolite. Some natural zeolites may sometimes be converted to zeolites of the desired type by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination. The zeolites preferably have a crystal framework density, in the dry hydrogen form, not substantially below about 1.6 g.cm⁻³. The dry density for known structures may be calculated from the number of silicon plus aluminum atoms per 1000 cubic Angstroms, as given, e.g., on page 19 of the article on Zeolite Structure by W. M. Meier included in "Proceedings of the Conference on Molecular Sieves, London, April 1967",

published by the Society of Chemical Industry, London, 1968. Reference is made to this paper for a discussion of the crystal framework density. A further discussion of crystal framework density, together with values for some typical zeolites, is given in U.S. Pat. No. 4,016,218, to which reference is made. When synthesized in the alkali metal form, the zeolite is conveniently converted to the hydrogen form, generally by intermediate formation of the ammonium form as a result of ammonium ion exchange and calcination of the ammonium form to yield the hydrogen form. It has been found that although the hydrogen form of the zeolite catalyzes the reaction successfully, the zeolite may also be partly in the alkali metal form.

Preferred zeolite catalysts include zeolite beta, HZSM-4, HZSM-20 and HZSM-38. Most preferred catalyst is acidic zeolite beta. A zeolite beta suitable for use herein is disclosed in US3,308,069 to which reference is made for details of this zeolite and its preparation.

Zeolite beta catalysts in the acid form are also commercially available as Zeocat PB/H from Zeochem. Other zeolite beta catalysts suitable for use can be provided by UOP Chemical Catalysts and Zeolyst International.

Most generally, alkylation catalysts may be used herein provided that the alkylation catalyst 1) can accommodate into the smallest pore diameter of said catalyst said branched olefins described herein and 2) selectively alkylate benzene with said branched olefins and/or mixture with nonbranched olefins with sufficient selectivity to provide the 2/3-Ph index values defined herein.

In one preferred mode, a hydrotrope or hydrotrope precursor is added either after step (I), during or after step (II) and prior to step (III) or during or after step (III). The hydrotropes are selected from any suitable hydrotrope, typically a sulfonic acid or sodium sulfonate salt of toluene, cumene, xylene, naphthalene or mixtures thereof. The hydrotropes precursors are selected from any suitable, hydrotrope precursor typically toluene, cumene, xylene, naphthalene or mixtures thereof.

Sulfonation and Workup or Neutralization (Steps II / III)

Preferably the sulfonating step (II) is performed using a sulfonating agent, preferably selected from the group consisting of sulfuric acid, sulfur trioxide with or without air, chlorosulfonic acid, oleum, and mixtures thereof. Furthermore, it is

preferable in step (II) to remove components other than monoalkylbenzene prior to contacting the product of step (I) with sulfonating agent.

In general, sulfonation of the modified alkylbenzenes in the instant process can be accomplished using any of the well-known sulfonation systems, including those described in "Detergent Manufacture Including Zeolite Builders and other New Materials", Ed. Sittig., Noyes Data Corp., 1979, as well as in Vol. 56 in "Surfactant Science" series, Marcel Dekker, New York, 1996, including in particular Chapter 2 entitled "Alkylarylsulfonates: History, Manufacture, Analysis and Environmental Properties", pages 39-108 which includes 297 literature references. This work provides access to a great deal of literature describing various processes and process steps, not only sulfonation but also dehydrogenation, alkylation, alkylbenzene distillation and the like. Common sulfonation systems useful herein include sulfuric acid, chlorosulfonic acid, oleum, sulfur trioxide and the like. Sulfur trioxide/air is especially preferred. Details of sulfonation using a suitable air/sulfur trioxide mixture are provided in US 3,427,342, Chemithon. Sulfonation processes are further extensively described in "Sulfonation Technology in the Detergent Industry", W.H. de Groot, Kluwer Academic Publishers, Boston, 1991.

Any convenient workup steps may be used in the present process. Common practice is to neutralize after sulfonation with any suitable alkali. Thus the neutralization step can be conducted using alkali selected from sodium, potassium, ammonium, magnesium and substituted ammonium alkalis and mixtures thereof. Potassium can assist solubility, magnesium can promote soft water performance and substituted ammonium can be helpful for formulating specialty variations of the instant surfactants. The invention encompasses any of these derivative forms of the modified alkylbenzenesulfonate surfactants as produced by the present process and their use in consumer product compositions.

Alternately the acid form of the present surfactants can be added directly to acidic cleaning products, or can be mixed with cleaning ingredients and then neutralized.

Preferably the neutralisation step (III) is performed using a basic salt. Preferably the basic salt having a cation selected from the group consisting of alkali metal, alkaline earth metal, ammonium, substituted ammonium, and mixtures thereof and an anion

selected from hydroxide, oxide, carbonate, silicate, phosphate and mixtures thereof. More preferably the basic salt is selected from the group consisting of sodium hydroxide, potassium hydroxide, magnesium hydroxide, calcium hydroxide, ammonium hydroxide, and mixtures thereof.

The processes are tolerant of variation, for example conventional steps can be added before, in parallel with, or after the outlined steps (I), (II) and (III). This is especially the case for accomodating the use of hydrotropes or their precursors.

Preparative Examples

EXAMPLE 1

Mixture of 4-methyl-4-nonanol, 5-methyl-5-decanol,
6-methyl-6-undecanol and 6-methyl-6-dodecanol

(A starting-material for branched olefins)

A mixture of 4.65 g of 2-pentanone, 20.7 g of 2-hexanone, 51.0 g of 2-heptanone, 36.7 g of 2-octanone and 72.6 g of diethyl ether is added to an addition funnel. The ketone mixture is then added dropwise over a period of 2.25 hours to a nitrogen blanketed stirred three neck 2 L round bottom flask, fitted with a reflux condenser and containing 600 mL of 2.0 M n-pentylmagnesium bromide in diethyl ether and an additional 400 mL of diethyl ether. After the addition is complete the reaction mixture is stirred an additional 2.5 hours at 20°C. The reaction mixture is then added to 1kg of cracked ice with stirring. To this mixture is added 393.3 g of 30% sulphuric acid solution. The aqueous acid layer is drained and the remaining ether layer is washed twice with 750 mL of water. The ether layer is then evaporated under vacuum to yield 176.1 g of a mixture of 4-methyl-4-nonanol, 5-methyl-5-decanol, 6-methyl-6-undecanol and 6-methyl-6-dodecanol.

EXAMPLE 2

Substantially Mono Methyl Branched Olefin Mixture With Randomized Branching

an alkylating agent for preparing
modified alkylbenzenes in accordance with the invention

- a) A 174.9 g sample of the mono methyl branched alcohol mixture of example 1 is added to a nitrogen blanketed stirred three neck round bottom 500 mL flask, fitted with a Dean Stark trap and a reflux condenser along with 35.8 g of a shape selective zeolite catalyst (acidic mordenite catalyst ZeocatTM FM-8/25H). With mixing, the mixture is then heated to about 110-155°C and water and some olefin is collected over a period of 4-5 hours in the Dean Stark trap. The conversion of the alcohol mixture of example 1 to a substantially non-randomized methyl branched olefin mixture is now complete and the reaction mixture is cooled to 20°C. The substantially non-randomized methyl branched olefin mixture remaining in the flask is filtered to remove catalyst. The solid filter cake is washed twice with 100 mL portions of hexane. The hexane filtrate is evaporated under vacuum and the resulting product is combined with the first filtrate to give 148.2 g of a substantially non-randomized methyl branched olefin mixture.
- b) The olefin mixture of example 2a is combined with 36g of a shape selective zeolite catalyst (acidic mordenite catalyst ZeocatTM FM-8/25H) and reacted according to example 2a with the following changes. The reaction temperature is raised to 190-200°C for a period of about 1-2 hours to randomize the specific branch positions in the olefin mixture. The reaction mixture is cooled to 20°C. The substantially mono methyl branched olefin mixture with randomized branching remaining in the flask is filtered to remove catalyst. The solid filter cake is washed twice with 100 mL portions of hexane. The hexane filtrate is evaporated under vacuum and the resulting product is combined with the first filtrate to give 147.5 g of a substantially mono methyl branched olefin mixture with randomized branching.

EXAMPLE 3

Substantially Mono Methyl Branched Alkylbenzene Mixture 2/3-Phenyl Index of about 200 and a 2-Methyl-2-Phenyl Index of About 0.005
(A modified alkylbenzene mixture in accordance with the invention)

147 g of the substantially mono methyl branched olefin mixture with randomized branching of example 2 and 36 g of a shape selective zeolite catalyst (acidic beta zeolite catalyst ZeocatTM PB/H) are added to a 2 gallon stainless steel, stirred autoclave. Residual olefin and catalyst in the container are washed into the autoclave with 300 mL

of n-hexane and the autoclave is sealed. From outside the autoclave cell, 2000 g of benzene (contained in a isolated vessel and added by way of an isolated pumping system inside the isolated autoclave cell) is added to the autoclave. The autoclave is purged twice with 250 psig N₂, and then charged to 60 psig N₂. The mixture is stirred and heated to about 200°C for about 4-6 hours. The autoclave is cooled to about 20°C overnight. The valve is opened leading from the autoclave to the benzene condenser and collection tank. The autoclave is heated to about 120°C with continuous collection of benzene. No more benzene is collected by the time the reactor reaches 120°C. The reactor is then cooled to 40°C and 750 g of n-hexane is pumped into the autoclave with mixing. The autoclave is then drained to remove the reaction mixture. The reaction mixture is filtered to remove catalyst and the n-hexane is evaporated under low vacuum. The product is then distilled under high vacuum (1-5 mm of Hg). The substantially mono methyl branched alkylbenzene mixture with a 2/3-Phenyl Index of about 200 and a 2-methyl-2-phenyl index of about 0.005 is collected from 76°C - 130°C (167 g).

EXAMPLE 4

Substantially Mono Methyl Branched Alkylbenzenesulfonic Acid Mixture

With a 2/3-Phenyl Index of about 200 and a 2-Methyl-2-Phenyl Index of About 0.005

(A modified alkylbenzene sulfonic acid mixture in accordance with the invention)

The product of example 3 is sulfonated with a molar equivalent of chlorosulfonic acid using methylene chloride as solvent. The methylene chloride is removed to give 210 g of a substantially mono methyl branched alkylbenzenesulfonic acid mixture with a 2/3-Phenyl Index of about 200 and a 2-methyl-2-phenyl index of about 0.005.

EXAMPLE 5

Substantially Mono Methyl Branched Alkylbenzenesulfonate, Sodium Salt Mixture

With a 2/3-Phenyl Index of about 200 and 2-Methyl-2-Phenyl Index of About 0.005

(A modified alkylbenzene sulfonate surfactant mixture in accordance with the invention)

The product of example 4 is neutralized with a molar equivalent of sodium methoxide in methanol and the methanol is evaporated to give 225 g of a substantially mono methyl

branched alkylbenzenesulfonate, sodium salt mixture with a 2/3-Phenyl Index of about 200 and a 2-methyl-2-phenyl index of about 0.005

EXAMPLE 6

Substantially Linear Alkylbenzene Mixture

With a 2/3-Phenyl Index of About 200 and a 2-Methyl-2-Phenyl Index of about 0.02.

(An alkylbenzene mixture used as a component of modified alkylbenzenes)

A mixture of chain lengths of substantially linear alkylbenzenes with a 2/3-Phenyl Index of about 200 and a 2-methyl-2-phenyl index of about 0.02 is prepared using a shape zeolite catalyst (acidic beta zeolite catalyst ZeocatTM PB/H). A mixture of 15.1 g of Neodene (R)10, 136.6 g of Neodene(R)1112, 89.5 g of Neodene(R)12 and 109.1 g of 1-tridecene is added to a 2 gallon stainless steel, stirred autoclave along with 70 g of a shape selective catalyst (acidic beta zeolite catalyst ZeocatTM PB/H). Neodene is a trade name for olefins from Shell Chemical Company. Residual olefin and catalyst in the container are washed into the autoclave with 200 mL of n-hexane and the autoclave is sealed. From outside the autoclave cell, 2500 benzene (contained in a isolated vessel and added by way of an isolated pumping system inside the isolated autoclave cell) is added to the autoclave. The autoclave is purged twice with 250 psig N₂, and then charged to 60 psig N₂. The mixture is stirred and heated to 170°C to 175°C for about 18 hours then cooled to 70-80°C. The valve is opened leading from the autoclave to the benzene condenser and collection tank. The autoclave is heated to about 120°C with continuous collection of benzene in collection tank. No more benzene is collected by the time the reactor reaches 120°C. The reactor is then cooled to 40°C and 1 kg of n-hexane is pumped into the autoclave with mixing. The autoclave is then drained to remove the reaction mixture. The reaction mixture is filtered to remove catalyst and the n-hexane is evaporated under low vacuum. The product is then distilled under high vacuum (1-5 mm of Hg). The substantially linear alkylbenzene mixture with a 2/3-Phenyl Index of about 200 and a 2-methyl-2-phenyl index of about 0.02 is collected from 85°C - 150°C (426.2 g).

EXAMPLE 7

Substantially Linear Alkylbenzenesulfonic Acid Mixture

With a 2/3-Phenyl Index of About 200 and a 2-Methyl-2-Phenyl Index of about 0.02

(An alkylbenzenesulfonic acid mixture to be used as a component of modified alkylbenzenesulfonic acid in accordance with the invention)

422.45 g of the product of example 6 is sulfonated with a molar equivalent of chlorosulfonic acid using methylene chloride as solvent. The methylene chloride is removed to give 574 g of a substantially linear alkylbenzenesulfonic acid mixture with a 2/3-Phenyl Index of about 200 and a 2-methyl-2-phenyl index of about 0.02.

EXAMPLE 8

Substantially Linear Alkylbenzene Sulfonic Acid Mixture

With a 2/3-Phenyl Index of About 200 and a 2-Methyl-2-Phenyl Index of About 0.02

(An alkylbenzenesulfonate surfactant mixture to be used as a component of modified alkylbenzenesulfonate surfactant mixtures in accordance with the invention)

The substantially linear alkylbenzene sulfonic acid mixture of example 7 is neutralized with a molar equivalent of sodium methoxide in methanol and the methanol is evaporated to give 613 g of the substantially linear alkylbenzene sulfonate, sodium salt mixture with a 2/3-Phenyl Index of about 200 and a 2-methyl-2-phenyl index of about 0.02.

EXAMPLE 9

6,10-Dimethyl-2-undecanol

(A starting-material for branched olefins)

To a glass autoclave liner is added 299 g of geranylacetone, 3.8 g or 5% ruthenium on carbon and 150 ml of methanol. The glass liner is sealed inside a 3 L, stainless steel, rocking autoclave and the autoclave purged once with 250 psig N₂, once with 250 psig H₂ and then charged with 1000 psig H₂. With mixing, the reaction mixture is heated. At about 75°C, the reaction initiates and begins consuming H₂ and exotherms to 170-180°C. In 10-15 minutes, the temperature has dropped to 100-110°C and the pressure dropped to 500 psig. The autoclave is boosted to 1000 psig with H₂ and mixed at 100-110°C for an additional 1 hour and 40 minutes with the reaction consuming an additional 160 psig H₂.

but at which time no more H₂ consumption is observed. Upon cooling the autoclave to 40°C, the reaction mixture removed, filtered to remove catalyst and concentrated by evaporation of methanol under vacuum to yield 297.75 g of 6,10-dimethyl-2-undecanol.

EXAMPLE 10

5,7-Dimethyl-2-decanol

(A starting-material for branched olefins)

To a glass autoclave liner is added 249 g of 5,7-dimethyl-3,5,9-decatrien-2-one, 2.2 g or 5% ruthenium on carbon and 200 ml of methanol. The glass liner is sealed inside a 3 L, stainless steel, rocking autoclave and the autoclave purged once with 250 psig N₂, once with 250 psig H₂ and then charged with 500 psig H₂. With mixing, the reaction mixture is heated. At about 75°C, the reaction initiates and begins consuming H₂ and exotherms to 170°C. In 10 minutes, the temperature has dropped to 115-120°C and the pressure dropped to 270 psig. The autoclave is boosted to 1000 psig with H₂, mixed at 110-115°C for an additional 7 hours and 15 minutes then cooled to 30°C. The reaction mixture is removed from autoclave, filtered to remove catalyst and concentrated by evaporation of methanol under vacuum to yield 225.8 g of 5,7-dimethyl-2-decanol.

EXAMPLE 11

4,8-Dimethyl-2-nonanol

(A starting-material for branched olefins)

A mixture of 671.2 g of citral and 185.6 g of diethyl ether is added to an addition funnel. The citral mixture is then added dropwise over a five hour period to a nitrogen blanketed, stirred, 5 L, 3-neck, round bottom flask equipped with a reflux condenser containing 1.6 L of 3.0 M methylmagnesium bromide solution and an additional 740 ml of diethyl ether. The reaction flask is situated in an ice water bath to control exotherm and subsequent ether reflux. After addition is complete, the ice water bath is removed and the reaction allowed to mix for an additional 2 hours at 20-25°C at which point the reaction mixture is added to 3.5 Kg of cracked ice with good mixing. To this mixture is added 1570 g of 30% sulfuric acid solution. The aqueous acid layer is drained and the remaining ether layer washed twice with 2 L of water. The ether layer is concentrated by evaporation of

the ether under vacuum to yield 720.6 g of 4,8-dimethyl-3,7-nonadien-2-ol. To a glass autoclave liner is added 249.8 g of the 4,8-dimethyl-3,7-nonadien-2-ol, 5.8 g or 5% palladium on activated carbon and 200 ml of n-hexane. The glass liner is sealed inside a 3 L, stainless steel, rocking autoclave and the autoclave purged twice with 250 psig N₂, once with 250 psig H₂ and then charged with 100 psig H₂. Upon mixing, the reaction initiates and begins consuming H₂ and exotherms to 75°C. The autoclave is heated to 80°C, boosted to 500 psig with H₂, mixed for 3 hours and then cooled to 30°C. The reaction mixture is removed from autoclave, filtered to remove catalyst and concentrated by evaporation of n-hexane under vacuum to yield 242 g of 4,8-dimethyl-2-nonanol.

EXAMPLE 12

Substantially Dimethyl Branched Olefin Mixture With Randomized Branching
(A branched olefin mixture which is an alkylating agent for preparing modified alkylbenzenes in accordance with the invention)

To a nitrogen blanketed, 2 L, 3-neck round bottom flask equipped with thermometer, mechanical stirrer and a Dean-Stark trap with reflux condenser is added 225 g of 4,8-dimethyl-2-nonanol (example 11), 450 g of 5,7-dimethyl-2-decanol (example 10), 225 g of 6,10-dimethyl-2-undecanol (example 9) and 180 g of a shape selective zeolite catalyst (acidic mordenite catalyst Zeocat™ FM-8/25H). With mixing, the mixture is heated (135-160°C) to the point water and some olefin is driven off and collected in Dean-Stark trap at a moderate rate. After a few hours, the rate of water collection slows and the temperature rises to 180-195°C where the reaction is allowed to mix for an additional 2-4 hours. The dimethyl branched olefin mixture remaining in the flask is filtered to remove the catalyst. The catalyst filter cake is slurried with 500 ml of hexane and vacuum filtered. The catalyst filter cake is washed twice with 100 ml of hexane and the filtrate concentrated by evaporation of the hexane under vacuum. The resulting product is combined with the first filtrate to give 820 g of dimethyl branched olefin mixture with randomized branching.

EXAMPLE 13

Substantially Dimethyl Branched Alkylbenzene Mixture With Randomized Branching
and 2/3-Phenyl Index of About 200 and a 2-Methyl-2-Phenyl Index of About 0.04

(A modified alkylbenzene mixture in accordance with the invention)

820 g of the dimethyl branched olefin mixture of example 12 and 160 g of a shape selective zeolite catalyst (acidic beta zeolite catalyst ZeocatTM PB/H) are added to a 2 gallon stainless steel, stirred autoclave and the autoclave is sealed. The autoclave is purged twice with 80 psig N₂ and then charged to 60 psig N₂. From outside the autoclave cell, 3000 g of benzene (contained in a isolated vessel and added by way of an isolated pumping system inside the isolated autoclave cell) is added to the autoclave. The mixture is stirred and heated to about 205°C for about 8 hours. The autoclave is cooled to about 30°C overnight. The valve is opened leading from the autoclave to the benzene condenser and collection tank. The autoclave is heated to about 120°C with continuous collection of benzene. No more benzene is collected by the time the reactor reaches 120°C and the reactor is then cooled to 40°C. The autoclave is then drained to remove the reaction mixture. The reaction mixture is filtered to remove catalyst and vacuum pulled on the mixture to remove any residual traces of benzene. The product is distilled under vacuum (1-5 mm of Hg). The dimethyl branched alkylbenzene mixture with randomized branching and 2/3-Phenyl Index of about 200 and a 2-methyl-2-phenyl index of about 0.04 is collected from 88°C - 160°C.

EXAMPLE 14

Substantially Dimethyl Branched Alkylbenzenesulfonic Acid Mixture With Randomized
Branching and a 2/3-Phenyl Index of About 200
and 2-Methyl-2-Phenyl Index of About 0.04

(A modified alkylbenzenesulfonic acid mixture in accordance with the invention)

The dimethyl branched alkylbenzene product of example 13 is sulfonated with a molar equivalent of chlorosulfonic acid using methylene chloride as solvent with HCl evolved as a side product. The resulting sulfonic acid product is concentrated by evaporation of methylene chloride under vacuum. The resulting sulfonic acid product has a 2/3-Phenyl Index of about 200 and a 2-methyl-2-phenyl index of about 0.04.

EXAMPLE 15

Substantially Dimethyl Branched Alkylbenzene Sulfonic Acid, Sodium Salt Mixture with
Randomized Branching and 2/3-Phenyl Index of About 200
and a 2-Methyl-2-Phenyl Index of About 0.04

(A modified alkylbenzenesulfonate surfactant mixture in accordance with the invention)

The dimethyl branched alkylbenzenesulfonic acid mixture of example 14 is neutralized with a molar equivalent of sodium methoxide in methanol and the methanol is evaporated to give solid dimethyl branched alkylbenzene sulfonate, sodium salt mixture with randomized branching and a 2/3-Phenyl Index of about 200 and a 2-methyl-2-phenyl index of about 0.04.

EXAMPLE 16

Mixture of Linear and Branched Alkylbenzenes

With a 2/3-Phenyl Index of About 200 and a 2-Methyl-2-Phenyl Index of About 0.01

(A modified alkylbenzene mixture in accordance with the invention)

A modified alkylbenzene mixture is prepared by combining 147.5 g of the product of example 3 and 63.2 g of the product of example 6. The resulting modified alkylbenzene mixture has a 2/3-phenyl index of about 200 and a 2-Methyl-2-phenyl Index of about 0.01.

EXAMPLE 17

Mixture of Linear and Branched Alkylbenzenesulfonic Acid and Salts

With a 2/3-Phenyl Index of About 200 and a 2-Methyl-2-Phenyl Index of About 0.01

(modified alkylbenzenesulfonic acid mixtures and salt mixtures of the invention)

a) Modified Alkylbenzenesulfonic Acid Mixture of the Invention

The resulting modified alkylbenzene mixture of example 16 is sulfonated with a molar equivalent of chlorosulfonic acid using methylene chloride as solvent with HCl evolved as a side product. The resulting sulfonic acid product is concentrated by evaporation of methylene chloride under vacuum. The resulting modified alkylbenzenesulfonic acid product has a 2/3-Phenyl Index of about 200 and a 2-methyl-2-phenyl index of about 0.01.

b) Modified Alkylbenzenesulfonate, Sodium Salt Mixture of the Invention

The product of example 17a) is neutralized with a molar equivalent of sodium methoxide in methanol and the methanol is evaporated to give solid modified alkylbenzenesulfonate, sodium salt mixture of the invention with a 2/3-Phenyl Index of about 200 and a 2-methyl-2-phenyl index of about 0.01.

Methods for Determining Compositional Parameters (2/3-phenyl index, 2-methyl-2-phenyl index) of Mixed Alkylbenzene/ Alkylbenzenesulfonate/ Alkylbenzenesulfonic Acid Systems.

It is well known in the art to determine compositional parameters of conventional linear alkylbenzenes and/or highly branched alkylbenzenesulfonates (TPBS, ABS). See, for example Surfactant Science Series, Volume 40, Chapter 7 and Surfactant Science Series, Volume 73, Chapter 7. Typically this is done by GC and/or GC-mass spectroscopy for the alkylbenzenes and HPLC for the alkylbenzenesulfonates or sulfonic acids; ¹³C nmr is also commonly used. Another common practice is desulfonation. This permits GC and/or GC-mass spectroscopy to be used, since desulfonation converts the sulfonates or sulfonic acids to the alkylbenzenes which are tractable by such methods.

In general, the present invention provides unique and relatively complex mixtures of alkylbenzenes, and similarly complex surfactant mixtures of alkylbenzenesulfonates and/or alkylbenzenesulfonic acids. Compositional parameters of such compositions can be determined using variations and combinations of the art-known methods.

The sequence of methods to be used depends on the composition to be characterized as follows:

Composition to be characterized	Sequence of Methods (Methods separated by commas are run in sequence, others can be run in parallel)
Alkylbenzene mixtures	GC, NMR1 NMR 2
Alkylbenzene mixtures with impurities*	GC, DIS, GC, NMR1 NMR 2
Alkylbenzenesulfonic acid	Option 1: HPLC, NMR3 NMR 4

mixtures	Option 2: HPLC, DE, NMR1 NMR 2
Alkylbenzenesulfonate salt mixtures	Option 1: HPLC, AC, NMR3 NMR 4 Option 2: HPLC, DE, NMR1 NMR 2
Alkylbenzenesulfonic acid mixtures with impurities*	Option 1: HPLC, HPLC-P, HPLC, NMR3 NMR 4 Option 2: HPLC, DE, DIS, GC, NMR1 NMR 2
Alkylbenzenesulfonate salt mixtures with impurities*	Option 1: HPLC, HPLC-P, HPLC, AC, NMR3 NMR 4 Option 2: HPLC, DE, DIS, GC, NMR1 NMR 2

* Typically preferred when the material contains more than about 10% impurities such as dialkylbenzenes, olefins, paraffins, hydrotropes, dialkylbenzenesulfonates, etc.

GC

Equipment:

- Hewlett Packard Gas Chromatograph HP5890 Series II equipped with a split/splitless injector and FID
- J&W Scientific capillary column DB-1HT, 30 meter, 0.25mm id, 0.1um film thickness cat# 1221131
- Restek Red lite Septa 11mm cat# 22306
- Restek 4mm Gooseneck inlet sleeve with a carbofit cat# 20799-209.5
- O-ring for inlet liner Hewlett Packard cat# 5180-4182
- J.T.Baker HPLC grade Methylene Chloride cat# 9315-33, or equivalent
- 2ml GC autosampler vials with crimp tops, or equivalent

Sample Preparation:

- Weigh 4-5 mg of sample into a 2 ml GC autosampler vial
- Add 1 ml J.T. Baker HPLC grade Methylene Chloride, cat# 9315-33 to the GC vial, seal with 11mm crimp vial teflon lined closures (caps), part # HP5181-1210 using crimper tool, part # HP8710-0979 and mix well
- The sample is now ready for injection into the GC

GC Parameters:

Carrier Gas: Hydrogen

Column Head Pressure: 9 psi

Flows: Column Flow @ 1 ml/min.

Split Vent @ ~3ml/min.

Septum Purge @ 1 ml/min.

Injection: HP 7673 Autosampler, 10 ul syringe, 1ul injection

Injector Temperature: 350 °C

Detector Temperature: 400 °C

Oven Temperature Program: initial 70 °C hold 1 min.

rate 1 °C/min.

final 180 °C hold 10 min.

Standards required for this method are 2-phenyloctane and 2-phenylpentadecane, each freshly distilled to a purity of greater than 98%. Run both standards using the conditions specified above to define the retention time for each standard. This defines a retention time range which is the retention time range to be used for characterizing any alkylbenzenes or alkylbenzene mixtures in the context of this invention (e.g., test samples). Now run the test samples for which compositional parameters are to be determined. Test samples pass the GC test provided that greater than 90% of the total GC area percent is within the retention time range defined by the two standards. Test samples that pass the GC test can be used directly in the NMR1 and NMR2 test methods. Test samples that do not pass the GC test must be further purified by distillation until the test sample passes the GC test.

DESULFONATION (DE)

The desulfonation method is a standard method described in "The Analysis of Detergents and Detergent Products" by G. F. Longman on pages 197-199. Two other useful descriptions of this standard method are given on page 230-231 of volume 40 of the Surfactant Science Series edited by T. M. Schmitt: "Analysis of Surfactants" and on page 272 of volume 73 of the Surfactant Science Series: "Anionic Surfactants" edited by John Cross. This is an alternative method to the HPLC method, described herein, for evaluation of the branched and nonbranched alkylbenzenesulfonic acid and/or salt mixtures (Modified Alkylbenzensulfonic acid and or salt Mixtures). The method

provides a means of converting the sulfonic acid and/or salt mixture into branched and nonbranched alkylbenzene mixtures which can then be analyzed by means of the GC and NMR methods NMR1 and NMR2 described herein.

HPLC

S. R. Ward, Anal. Chem., 1989, 61, 2534; D. J. Pietrzyk and S. Chen, Univ. Iowa, Dept. of Chemistry.

Apparatus

<u>Suitable HPLC System</u>	Waters Division of Millipore or equivalent.
HPLC pump with He sparge and temperature control	Waters, model 600 or equivalent
Autosampler/injector	Waters 717, or equivalent
Autosampler 48 position tray	Waters or equivalent
UV detector	Waters PDA 996 or equivalent
Fluorescence detector	Waters 740 or equivalent
Data System/Integrator	Waters 860 or equivalent
Autosampler vials and caps	4 mL capacity, Millipore #78514 and #78515.
HPLC Column, X2	Supelcosil LC18, 5 µm, 4.6 mm x 25 cm, Supelcosil #58298
Column Inlet Filter	Rheodyne 0.5um x 3 mm Rheodyne #7335
LC eluent membrane filters	Millipore SJHV M47 10, disposable filter funnel with 0.45 µm membrane.
Balance	Sartorius or equivalent; precision ±0.0001g.
Vacuum	Sample Clarification Kit with pumps and filters, Waters #WAT085113.

Reagents

C8 LAS standard material	Sodium-p-2-octylbenzene sulfonate.
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Procedure

A. Preparation of HPLC mobile Phase

1. Mobile phase A
 - a) Weigh 11.690 g sodium chloride and transfer to a 2000 mL volumetric flask. Dissolve in 200 mL HPLC grade water.
 - b) Add 800 mL of acetonitrile and mix. Dilute to volume after solution comes to room temperature. This prepares a solution of 100 mM NaCl/40% ACN.
 - c) Filter through an LC eluent membrane filter and degas prior to use.

2. Mobile phase B - Prepare 2000 mL of 60% acetonitrile in HPLC grade water. Filter through an LC eluent membrane filter and degas prior to use.

B. C8 and C15 Internal Standard Solution

1. Weigh 0.050 g of a 2-phenyloctylbenzenesulfonate and 0.050g of 2-Phenylpentadecanesulfonate standards and quantitatively transfer to a 100 mL volumetric flask.
 2. Dissolve with 30 mL ACN and dilute to volume with HPLC grade water. This prepares ca. 1500 ppm solution of the mixed standard.

C. Sample Solutions

1. Wash Solutions - Transfer 250 μ L of the standard solution to a 1 mL autosampler vial and add 750 μ L of the wash solution. Cap and place in the autosampler tray.
 2. Alkylbenzenesulfonic acid or Alkylbenzenesulfonate - Weigh 0.10 g of the alkylbenzenesulfonic acid or salt and quantitatively transfer to a 100 mL volumetric flask. Dissolve with 30 mL ACN and dilute to volume with HPLC grade water. Transfer 250 μ L of the standard solution to a 1 mL autosampler vial and add 750 μ L of the sample solution. Cap and place in the autosampler tray. If solution is excessively turbid, filter through 0.45 μ m membrane before transferring to auto-sampler vial. Cap and place in the auto-sampler tray.

D. HPLC System

1. Prime HPLC pump with mobile phase. Install column and column inlet filter and equilibrate with eluent (0.3 mL/min for at least 1 hr.).

2. Run samples using the following HPLC conditions:

Mobile phase A 100 mM NaCl/40% ACN

Mobile phase B 40% H₂O/60% ACN

time 0 min. 100% Mobile phase A 0% Mobile Phase B

time 75 min. 5% Mobile phase A 95% Mobile Phase B

time 98 min. 5% Mobile phase A 95% Mobile Phase B

time 110 min. 100% Mobile phase A 0% Mobile Phase B

time 120 min. 100% Mobile phase A 0% Mobile Phase B

Note: A gradient delay time of 5-10 minutes may be needed depending on dead volume of HPLC system.

Flow rate 1.2 mL/min.

Temperature 25°C

He sparge rate 50 mL/hr.

UV detector 225 nm

Fluorescence detector $\lambda = 225$ nm, $\lambda = 295$ nm with sensitivity at 10 x.

Run time 120 min.

Injection volume 10 μ L

Replicate injections 2

Data rate 0.45 MB/Hr.

Resolution 4.8nm

3. The column should be washed with 100% water followed by 100% acetonitrile and stored in 80/20 ACN/water.

The HPLC elution time of the 2-phenyloctylbenzenesulfonate defines the lower limit and the elution time of the 2-phenylpentadecanesulfonate standard defines the upper limit of the HPLC analysis relating to the alkylbenzenesulfonic acid/salt mixture of the invention. If 90% of the alkylbenzenesulfonic acid/salt mixture components have retention times within the range of the above standards then the sample can be further defined by methods NMR 3 and NMR 4.

If the alkylbenzenesulfonic acid/salt mixture contains 10% or more of components outside the retention limits defined by the standards then the mixture should be further purified by method HPLC-P or by DE, DIS methods.

HPLC Preparative (HPLC-P)

Alkylbenzenesulfonic acids and/or the salts which contain substantial impurities (10% or greater) are purified by preparative HPLC. See, for example Surfactant Science Series, Volume 40, Chapter 7 and Surfactant Science Series, Volume 73, Chapter 7. This is routine to one skilled in the art. A sufficient quantity should be purified to meet the requirements of the NMR 3 and NMR 4.

DISTILLATION (DIS)

A 5 liter, 3-necked round bottom flask with 24/40 joints is equipped with a magnetic stir bar. A few boiling chips (Hengar Granules, catalog #136-C) are added to the flask. A 9 1/2 inch long vigreux condenser with a 24/40 joint is placed in the center neck of the flask. A water cooled condenser is attached to the top of the vigreux condenser which is fitted with a calibrated thermometer. A vacuum receiving flask is attached to the end of the condenser. A glass stopper is placed in one side arm of the 5 liter flask and a calibrated thermometer in the other. The flask and the vigreux condenser are wrapped with aluminum foil. To the 5 liter flask, is added 2270 g of an alkylbenzene mixture which contains 10% or more impurities as defined by the GC method. A vacuum line leading from a vacuum pump is attached to the receiving flask. The alkylbenzene mixture in the 5 liter flask is stirred and vacuum is applied to the system. Once the maximum vacuum is reached (at least 1 inch of Hg pressure by gauge or less), the alkylbenzene mixture is heated by means of an electric heating mantle. The distillate is collected in two fractions. Fraction A is collected from about 25°C to about 90°C as measured by the calibrated thermometer at the top of the vigreux column. Fraction B is collected from about 90°C to about 155°C as measured by the calibrated thermometer at the top of the vigreux column. Fraction A and pot residues (high boiling) are discarded. Fraction B (1881 g) contains the alkylbenzene mixture of interest. The method can be scaled according to the practitioner's needs provided that sufficient quantity of the

alkylbenzene mixture remains after distillation for evaluation by NMR methods NMR1 and NMR2.

Preparative LC method using Mega Bond Elut Sep Pak® (HPLC-P)

Alkylbenzenesulfonic acids and/or the salts which contain substantial impurities (10% or greater) can also be purified by an LC method (also defined herein as HPLC-P).

This procedure is actually preferred over HPLC column prep purification.

As much as 500 mg of unpurified MLAS salts can be loaded onto a 10g(60ml) Mega Bond Elut Sep Pak® and with optimized chromatography the purified MLAS salt can be isolated and ready for freeze drying within 2 hours. A 100 mg sample of Modified alkylbenzenesulfonate salt can be loaded onto a 5g(20ml) Bond Elut Sep Pak and ready within the same amount of time.

A. Instrumentation

HPLC: Waters Model 600E gradient pump, Model 717 Autosampler, Water's Millennium PDA, Millenium Data Manager (v. 2.15)

Mega Bond Elut: C18 bonded phase, Varian 5g or 10g, PN:1225-6023, 1225-6031 with adaptors

HPLC Columns: Supelcosil LC-18 (X2), 250x4.6mm, 5mm; #58298

Analytical Balance: Mettler Model AE240, capable of weighing samples to ± 0.01 mg

B. Accessories

Volumetrics: glass, 10mL

Graduated Cylinder: 1L

HPLC Autosampler Vials: 4mL glass vials with Teflon caps and glass low volume inserts and pipette capable of accurately delivering 1, 2, and 5mL volumes

C. Reagents and Chemicals

Water (DI-H₂O): Distilled, deionized water from a Millipore, Milli-Q system or equivalent

Acetonitrile (CH₃CN): HPLC grade from Baker or equivalent Sodium Chloride Crystal Baker Analyzed or equivalent

D. HPLC Conditions

Aqueous Phase Preparation:

A: To 600mL of DI-H₂O contained in a 1L graduated cylinder, add 5.845 g of sodium chloride. Mix well and add 400 ml ACN. Mix well.

B: To 400ml of DI-H₂O contained in a 1L graduated cylinder, add 600ml ACN and mix well.

Reservoir A: 60/40, H₂O/CAN with salt and Reservoir B: 40/60, H₂O/ACN

Run Conditions: Gradient: 100% A for 75 min. 5%A/ 95% B for 98 min. 5%A/95% B for 110min. 100%A for 125min.

Column Temperature Not Thermostatted (i.e., room temp.)

HPLC Flow Rate 1.2mL/min

Injection Volume 10mL

Run Time 125 minutes

UV Detection 225nm

Conc. >4mg/ml

SEP PAK EQUILIBRATION (BOND ELUT, 5G)

1. Pass 10 ml of a solution containing 25/75 H₂O/ACN onto the sep pak by applying positive pressure with a 10 cc syringe at a rate of ~ 40 drops/min. Do not allow the sep pak to go dry.
2. Immediately pass 10ml (x3) of a solution containing 70/30 H₂O/ACN in the same manner as #1. Do not allow the sep pak to go dry. Maintain a level of solution (~1mm) at the head of the sep pak.
3. The sep pak is now ready for sample loading. MLAS

SAMPLE LOADING/ SEPARATION AND ISOLATION

4. Weigh <200 mg of sample into a 1 dram vial and add 2 ml of 70/30 H₂O/ACN. Sonicate and mix well.
5. Load sample onto Bond Elut and with positive pressure from a 10 cc syringe begin separation. Rinse vial with 1 ml (x2) portions of the 70/30 solution and load onto sep pak. Maintain ~1mm of solution at the head of the sep pak.
6. Pass 10 ml of 70/30 onto the Bond Elut with positive pressure from a 10 cc syringe at a rate of ~40 drops/min.
7. 4. Repeat this with 3 ml and 4 ml and collect effluent if interested in impurities.

MLAS ISOLATION AND COLLECTION

1. Pass 10 ml of solution containing 25/75 H₂O/ACN with positive pressure from a 10 cc syringe and collect effluent. Repeat this with another 10 ml and again with 5 ml. The isolated MLAS is now ready for freeze drying and subsequent characterization.
2. Rotovap until ACN is removed and freeze dry the remaining H₂O. Sample is now ready for chromatography.

Note: When incorporating the Mega Bond Elut Sep Pak (10 g version) up to 500 mg of sample can be loaded onto the sep pak and with solution volume adjustments, the effluent can be ready for freeze drying within 2 hours.

SEP PAK EQUILIBRATION (BOND ELUT, 10G)

1. Pass 20 ml of a solution containing 25/75 H₂O/ACN onto the sep pak using laboratory air or regulated cylinder air at a rate which will allow ~ 40 drops/min. You can not use positive pressure from a syringe because it is not sufficient to move the solution thru the sep pak. Do not allow the sep pak to go dry.
2. Immediately pass 20ml (x2) and an additional 10 ml of a solution containing 70/30 H₂O/ACN in the same manner as #1. Do not allow the sep pak to go dry. Maintain a level of solution (~1mm)at the head of the sep pak.
3. The sep pak is now ready for sample loading.

MLAS SAMPLE LOADING/SEPARATION AND ISOLATION

1. Weigh <500 mg of sample into a 2 dram vial and add 5 ml of 70/30 H₂O/ACN. Sonicate and mix well.
2. Load sample onto Bond Elut and with positive pressure from an air source begin separation. Rinse vial with 2 ml (x2) portions of the 70/30 solution and put onto the sep pak. Maintain ~1mm of solution at the head of the sep pak.
3. Pass 20 ml of 70/30 onto the Bond Elut with positive pressure from an air source at a rate of ~40 drops/min. Repeat this with 6 ml and 8 ml and collect effluent if interested in impurities.

MLAS ISOLATION AND COLLECTION

1. Pass 20 ml of solution containing 25/75 H₂O/ACN with positive pressure from an air source and collect effluent.

2. Repeat this with another 20 ml and again with 10 ml. This isolated fraction contains the pure MLAS.
3. The isolated MLAS is now ready for freeze drying and subsequent characterization.
4. Rotovap until ACN is removed and freeze dry the remaining H₂O. Sample is now ready for chromatography.

Note: Adjustments in organic modifier concentration may be necessary for optimum separation and isolation.

ACIDIFICATION (AC)

Salts of alkylbenzenesulfonic acids are acidified by common means such as reaction in a solvent with HCl or sulfuric acid or by use of an acidic resin such as Amberlyst 15. Acidification is routine to one skilled in the art. After acidifying remove all solvents, especially any moisture, so that the samples are anhydrous and solvent-free.

Note: For all of the below NMR test methods, the chemical shifts of the NMR spectrum are either externally or internally referenced to TMS in CDCl₃, i.e. chloroform.

NMR 1

¹³C-NMR 2/3-Phenyl Index for Alkylbenzene Mixtures

A 400 mg sample of an alkylbenzene mixture is dissolved in 1 ml of anhydrous deuterated chloroform containing 1% v/v TMS as reference and placed in a standard NMR tube. The ¹³C NMR is run on the sample on a 300 MHz NMR spectrometer using a 20 second recycle time, a 40° ¹³C pulse width and gated heteronuclear decoupling. At least 2000 scans are recorded. The region of the ¹³C NMR spectrum between about 145.00 ppm to about 150.00 ppm is integrated. The 2/3-Phenyl index of an alkylbenzene mixture is defined by the following equation:

$$\text{2/3-Phenyl Index} = (\text{Integral from about } 147.65 \text{ ppm to about } 148.05 \text{ ppm}) / (\text{Integral from about } 145.70 \text{ ppm to about } 146.15 \text{ ppm}) \times 100$$

NMR 2

¹³C-NMR 2-Methyl-2-Phenyl Index

A 400 mg sample of an anhydrous alkylbenzene mixture is dissolved in 1 ml of anhydrous deuterated chloroform containing 1% v/v TMS as reference and placed in a

standard NMR tube. The ^{13}C NMR is run on the sample on a 300 MHz NMR spectrometer using a 20 second recycle time, a 40° ^{13}C pulse width and gated heteronuclear decoupling. At least 2000 scans are recorded. The ^{13}C NMR spectrum region between about 145.00 ppm to about 150.00 ppm is integrated. The 2-methyl-2-phenyl index of an alkylbenzene mixture is defined by the following equation:

$$\text{2-methyl-2-phenyl index} = (\text{Integral from about } 149.35 \text{ ppm to about } 149.80 \text{ ppm}) / (\text{Integral from about } 145.00 \text{ ppm to about } 150.00 \text{ ppm}).$$

NMR 3

^{13}C -NMR 2/3-Phenyl Index for Alkylbenzenesulfonic Acid Mixtures

A 400 mg sample of an anhydrous alkylbenzenesulfonic acid mixture is dissolved in 1 ml of anhydrous deuterated chloroform containing 1% v/v TMS as reference and placed in a standard NMR tube. The ^{13}C NMR is run on the sample on a 300 MHz NMR spectrometer using a 20 second recycle time, a 40° ^{13}C pulse width and gated heteronuclear decoupling. At least 2000 scans are recorded. The ^{13}C NMR spectrum region between about 152.50 ppm to about 156.90 ppm is integrated. The 2/3-Phenyl Index of an alkylbenzenesulfonic acid mixture is defined by the following equation:

$$\text{2/3-Phenyl Index} = (\text{Integral from about } 154.40 \text{ to about } 154.80 \text{ ppm}) / (\text{Integral from about } 152.70 \text{ ppm to about } 153.15 \text{ ppm}) \times 100$$

NMR 4

^{13}C -NMR 2-Methyl-2-Phenyl Index for Alkylbenzenesulfonic Acid Mixtures

A 400 mg sample of an anhydrous alkylbenzenesulfonic acid mixture is dissolved in 1 ml of anhydrous deuterated chloroform containing 1% v/v TMS as reference and placed in a standard NMR tube. The ^{13}C NMR is run on the sample on a 300 MHz NMR spectrometer using a 20 second recycle time, a 40° ^{13}C pulse width and gated heteronuclear decoupling. At least 2000 scans are recorded. The ^{13}C NMR spectrum region between about 152.50 ppm to about 156.90 ppm is integrated. The 2-methyl-2-

phenyl Index for an alkylbenzenesulfonic acid mixture is defined by the following equation:

2-methyl-2-phenyl index = (Integral from about 156.40 ppm to about 156.65 ppm)/(Integral from about 152.50 ppm to about 156.90 ppm).

In one embodiment of the present invention, the hand dishwashing compositions are substantially free from alkylbenzene sulfonate surfactants other than the modified alkylbenzene sulfonate surfactant mixture. That is no alkylbenzene sulfonate surfactants other than the modified alkylbenzene sulfonate surfactant mixture are added to the detergent compositions.

In another embodiment of the present invention, the hand dishwashing compositions may contain as an additional surfactant at least about 0.1%, preferably no more than about 10%, more preferably no more than about 5%, more preferably still, no more than about 1%, of a commercial C₁₀-C₁₄ linear alkylbenzene sulfonate surfactant. It is further preferred that the commercial C₁₀-C₁₄ linear alkylbenzene sulfonate surfactant has a 2/3 phenyl index of from 75 to 160.

In another embodiment of the present inventions the hand dishwashing compositions may contain as an additional surfactant at least about 0.1%, preferably no more than about 10%, more preferably no more than about 5%, more preferably still, no more than about 1%, of a commercial highly branched alkylbenzene sulfonate surfactant. For example TPBS or tetrapropylbenzene sulfonate.

The present invention encompasses less preferred but sometimes useful embodiments for their normal purposes, such as the addition of useful hydrotrope precursors and/or hydrotropes, such as C₁-C₈ alkylbenzenes, more typically toluenes, cumenes, xylenes, naphthalenes, or the sulfonated derivatives of any such materials, minor amounts of any other materials, such as tribranched alkylbenzene sulfonate surfactants, dialkylbenzenes and their derivatives, dialkyl tetrailins, wetting agents, processing aids, and the like. It will be understood that, with the exception of hydrotropes, it will not be usual practice in the present invention to include any such materials. Likewise it will be understood that such materials, if and when they interfere

with analytical methods, will not be included in samples of compositions used for analytical purposes.

Numerous variations of the present hand dishwashing compositions are useful. Such variations include:

- the hand dishwashing composition which is substantially free from alkylbenzene sulfonate surfactants other than said modified alkylbenzene sulfonate surfactant mixture;
- the hand dishwashing composition which comprises, in said component (iii), at least about 0.1%, preferably no more than about 10%, more preferably no more than about 5%, more preferably still, no more than about 1%, of a commercial C₁₀-C₁₄ linear alkylbenzene sulfonate surfactant;
- the hand dishwashing composition which comprises, in said component (iii), at least about 0.1%, preferably no more than about 10%, more preferably no more than about 5%, more preferably still, no more than about 1%, of a commercial highly branched alkylbenzene sulfonate surfactant. (e.g., TPBS or tetrapropylbenzene sulfonate);
- the hand dishwashing composition which comprises, in said component (iii), a nonionic surfactant at a level of from about 0.5% to about 25% by weight of said detergent composition, and wherein said nonionic surfactant is a polyalkoxylated alcohol in capped or non-capped form having: - a hydrophobic group selected from linear C₁₀-C₁₆ alkyl, mid-chain C₁-C₃ branched C₁₀-C₁₆ alkyl, guerbet branched C₁₀-C₁₆ alkyl, and mixtures thereof and - a hydrophilic group selected from 1-15 ethoxylates, 1-15 propoxylates 1-15 butoxylates and mixtures thereof, in capped or uncapped form. (when uncapped, there is also present a terminal primary -OH moiety and when capped, there is also present a terminal moiety of the form -OR wherein R is a C₁-C₆ hydrocarbyl moiety, optionally comprising a primary or, preferably when present, a secondary alcohol.);
- the hand dishwashing composition which comprises, in said component (iii), an alkyl sulfate surfactant at a level of from about 0.5% to about 25% by weight of said detergent composition, wherein said alkyl sulfate surfactant has a hydrophobic group selected from linear C₁₀-C₁₈ alkyl, mid-chain C₁-C₃ branched

C₁₀-C₁₈ alkyl, guerbet branched C₁₀-C₁₈ alkyl, and mixtures thereof and a cation selected from Na, K and mixtures thereof;

- the hand dishwashing composition which comprises, in said component (iii), an alkyl(polyalkoxy)sulfate surfactant at a level of from about 0.5% to about 25% by weight of said detergent composition, wherein said alkyl(polyalkoxy)sulfate surfactant has - a hydrophobic group selected from linear C₁₀-C₁₆ alkyl, mid-chain C₁-C₃ branched C₁₀-C₁₆ alkyl, guerbet branched C₁₀-C₁₆ alkyl, and mixtures thereof and - a (polyalkoxy)sulfate hydrophilic group selected from 1-15 polyethoxysulfate, 1-15 polypropoxysulfate, 1-15 polybutoxysulfate, 1-15 mixed poly(ethoxy/propoxy/butoxy)sulfates, and mixtures thereof, in capped or uncapped form; and - a cation selected from Na, K and mixtures thereof;

It is preferred that when the hand dishwashing composition comprises an alkyl(polyalkoxy)sulfate surfactant which has a hydrophobic group selected from linear C₁₀-C₁₆ alkyl, mid-chain C₁-C₃ branched C₁₀-C₁₆ alkyl, guerbet branched C₁₀-C₁₆ alkyl, and mixtures thereof; and a (polyalkoxy)sulfate hydrophilic group selected from 1-15 polyethoxysulfate, 1-15 polypropoxysulfate, 1-15 polybutoxysulfate, 1-15 mixed poly(ethoxy/propoxy/butoxy)sulfates, and mixtures thereof, in capped or uncapped form; and a cation selected from Na, K and mixtures thereof.

It is preferred that when the hand dishwashing composition comprises a nonionic surfactant, it is a polyalkoxylated alcohol in capped or non-capped form has a hydrophobic group selected from linear C₁₀-C₁₆ alkyl, mid-chain C₁-C₃ branched C₁₀-C₁₆ alkyl, guerbet branched C₁₀-C₁₆ alkyl, and mixtures thereof; and a hydrophilic group selected from 1-15 ethoxylates, 1-15 propoxylates 1-15 butoxylates and mixtures thereof, in capped or uncapped form. When uncapped, there is also present a terminal primary -OH moiety and when capped, there is also present a terminal moiety of the form -OR wherein R is a C₁-C₆ hydrocarbyl moiety, optionally comprising a primary or, preferably when present, a secondary alcohol.

It is preferred that when the hand dishwashing composition comprises an alkyl sulfate surfactant which has a hydrophobic group selected from linear C₁₀-C₁₆ alkyl, mid-chain C₁-C₃ branched C₁₀-C₁₈ alkyl, guerbet branched C₁₀-C₁₆ alkyl, and mixtures thereof and a cation selected from Na, K and mixtures thereof.

The hand dishwashing compositions of the present invention can be used or applied by hand and/or can be applied in unitary or freely alterable dosage, or by automatic dispensing means. They can be used in aqueous or non-aqueous cleaning systems. They can have a wide range of pH, for example from about 2 to about 12 or higher, though alkaline detergent compositions having a pH of from about 8 to about 11 are among the preferred embodiments, and they can have a wide range of alkalinity reserve. Both high-foaming and low-foaming types are encompassed, as well as types for use in all known aqueous and non aqueous consumer product cleaning processes.

AQUEOUS BASED HEAVY DUTY LIQUID DETERGENTS

SURFACTANTS

The present invention also comprises aqueous based liquid detergent compositions. The aqueous liquid detergent compositions preferably comprise from about 10% to about 98%, preferably from about 30% to about 95%, by weight of an aqueous liquid carrier which is preferably water. Additionally, the aqueous liquid detergent compositions of the present invention comprise a surfactant system which preferably contains one or more detergents co-surfactants in addition to the branched surfactants disclosed above. The additional co-surfactants can be selected from nonionic detergents surfactant, anionic detergents surfactant, zwitterionic detergents surfactant, amine oxide detergents surfactant, and mixtures thereof. The surfactant system typically comprises from about 5% to about 70%, preferably from about 15% to about 30%, by weight of the detergent composition.

Anionic Surfactant

Anionic surfactants include C₁₁-C₁₈ alkyl benzene sulfonates (LAS) and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates (AS), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺) CH₃ and CH₃(CH₂)_y(CHOSO₃⁻M⁺) CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-C₁₈ glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters.

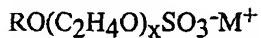
Generally speaking, anionic surfactants useful herein are disclosed in U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981, and in U.S. Patent No. 3,919,678, Laughlin et al, issued December 30, 1975.

Useful anionic surfactants include the water-soluble salts, particularly the alkali metal, ammonium and alkyloammonium (e.g., monoethanolammonium or triethanolammonium) salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of aryl groups.) Examples of this group of synthetic surfactants are the alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil.

Other anionic surfactants herein are the water-soluble salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 4 units of ethylene oxide per molecule and from about 8 to about 12 carbon atoms in the alkyl group.

Other useful anionic surfactants herein include the water-soluble salts of esters of a-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and α -alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Particularly preferred anionic surfactants herein are the alkyl polyethoxylate sulfates of the formula



wherein R is an alkyl chain having from about 10 to about 22 carbon atoms, saturated or unsaturated, M is a cation which makes the compound water-soluble, especially an alkali metal, ammonium or substituted ammonium cation, and x averages from about 1 to about 15.

Preferred alkyl sulfate surfactants are the non-ethoxylated C₁₂-15 primary and secondary alkyl sulfates. Under cold water washing conditions, i.e., less than about 65°F (18.3°C), it is preferred that there be a mixture of such ethoxylated and non-ethoxylated alkyl sulfates. Examples of fatty acids include capric, lauric, myristic, palmitic, stearic, arachidic, and behenic acid. Other fatty acids include palmitoleic, oleic, linoleic, linolenic, and ricinoleic acid.

Nonionic Surfactant

Conventional nonionic and amphoteric surfactants include C₁₂-C₁₈ alkyl ethoxylates (AE) including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy). The C₁₀-

C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Examples of nonionic surfactants are described in U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981.

Preferred examples of these surfactants include ethoxylated alcohols and ethoxylated alkyl phenols of the formula R(OC₂H₄)_nOH, wherein R is selected from the group consisting of aliphatic hydrocarbon radicals containing from about 8 to about 15 carbon atoms and alkyl phenyl radicals in which the alkyl groups contain from about 8 to about 12 carbon atoms, and the average value of n is from about 5 to about 15. These surfactants are more fully described in U.S. Patent No. 4,284,532, Leikhim et al, issued August 18, 1981. Particularly preferred are ethoxylated alcohols having an average of from about 10 to about 15 carbon atoms in the alcohol and an average degree of ethoxylation of from about 6 to about 12 moles of ethylene oxide per mole of alcohol. Mixtures of anionic and nonionic surfactants are especially useful.

Other conventional useful surfactants are listed in standard texts, including C₁₂-C₁₈ betaines and sulfobetaines (sultaines).

Amine Oxide Surfactants

The compositions herein also contain amine oxide surfactants of the formula:



In general, it can be seen that the structure (I) provides one long-chain moiety R¹(EO)_x(PO)_y(BO)_z and two short chain moieties, CH₂R'. R' is preferably selected from hydrogen, methyl and -CH₂OH. In general R¹ is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated, preferably, R¹ is a primary alkyl moiety. When x+y+z = 0, R¹ is a hydrocarbyl moiety having chainlength of from about 8 to about 18. When x+y+z is different from 0, R¹ may be somewhat longer, having a chainlength in the range C₁₂-C₂₄. The general formula also encompasses amine oxides wherein x+y+z = 0, R¹ = C₈-C₁₈, R' is H and q is 0-2, preferably 2. These amine oxides are illustrated by C₁₂-14 alkyldimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide and their hydrates, especially the dihydrates as disclosed in U.S. Patents 5,075,501 and 5,071,594, incorporated herein by reference.

The invention also encompasses amine oxides wherein x+y+z is different from zero, specifically x+y+z is from about 1 to about 10, R¹ is a primary alkyl group containing 8

to about 24 carbons, preferably from about 12 to about 16 carbon atoms; in these embodiments $y + z$ is preferably 0 and x is preferably from about 1 to about 6, more preferably from about 2 to about 4; EO represents ethyleneoxy; PO represents propyleneoxy; and BO represents butyleneoxy. Such amine oxides can be prepared by conventional synthetic methods, e.g., by the reaction of alkylethoxysulfates with dimethylamine followed by oxidation of the ethoxylated amine with hydrogen peroxide.

Highly preferred amine oxides herein are solids at ambient temperature, more preferably they have melting-points in the range 30°C to 90°C. Amine oxides suitable for use herein are made commercially by a number of suppliers, including Akzo Chemie, Ethyl Corp., and Procter & Gamble. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers. Preferred commercially available amine oxides are the solid, dihydrate ADMOX 16 and ADMOX 18, ADMOX 12 and especially ADMOX 14 from Ethyl Corp.

Preferred embodiments include dodecyldimethylamine oxide dihydrate, hexadecyldimethylamine oxide dihydrate, octadecyldimethylamine oxide dihydrate, hexadecyltris(ethyleneoxy)dimethyl-amine oxide, tetradecyldimethylamine oxide dihydrate, and mixtures thereof.

Whereas in certain of the preferred embodiments R' is H, there is some latitude with respect to having R' slightly larger than H. Specifically, the invention further encompasses embodiments wherein R' is CH₂OH, such as hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbis(2-hydroxyethyl)amine oxide.

Builders

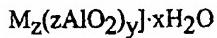
The compositions herein also optionally, but preferably, contain up to about 50%, more preferably from about 1% to about 40%, even more preferably from about 5% to about 30%, by weight of a detergent builder material. Lower or higher levels of builder, however, are not meant to be excluded. Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils. Detergent builders are described in U.S. Patent No. 4,321,165, Smith et al, issued March 23, 1982. Preferred builders for use in liquid detergents herein are described in U.S. Patent No. 4,284,532, Leikhim et al, issued August 18, 1981.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO₂:Na₂O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck.

NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na₂SiO₅ morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula NaMSi_xO_{2x+1}·yH₂O wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na₂SiO₅ (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a stabilizing agent for oxygen bleaches and as a component of suds control systems.

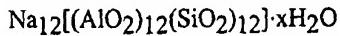
Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders can be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups,

preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

OTHER OPTIONAL COMPOSITION COMPONENTS

In addition to the liquid and solid phase components as hereinbefore described, the aqueous based detergent compositions can, and preferably will, contain various other optional components. Such optional components may be in either liquid or solid form. The optional components may either dissolve in the liquid phase or may be dispersed within the liquid phase in the form of fine particles or droplets. Some of the other materials which may optionally be utilized in the compositions herein are described in greater detail as follows:

Optional Inorganic Detergent Builders

The detergent compositions herein may also optionally contain one or more types of inorganic detergent builders beyond those listed hereinbefore that also function as alkalinity sources. Such optional inorganic builders can include, for example, aluminosilicates such as zeolites. Aluminosilicate zeolites, and their use as detergent builders are more fully discussed in Corkill et al., U.S. Patent No. 4,605,509; Issued August 12, 1986, the disclosure of which is incorporated herein by reference. Also crystalline layered silicates, such as those discussed in this '509 U.S. patent, are also suitable for use in the detergent compositions herein. If utilized, optional inorganic detergent builders can comprise from about 2% to 15% by weight of the compositions herein.

Optional Enzymes

The detergent compositions herein may also optionally contain one or more types of detergent enzymes. Such enzymes can include proteases, amylases, cellulases and lipases. Such materials are known in the art and are commercially available. They may be incorporated into the non-aqueous liquid detergent compositions herein in the form of suspensions, "marumes" or "prills". Another suitable type of enzyme comprises those in the form of slurries of enzymes in nonionic surfactants, e.g., the enzymes marketed by

Novo Nordisk under the tradename "SL" or the microencapsulated enzymes marketed by Novo Nordisk under the tradename "LDP."

Enzymes added to the compositions herein in the form of conventional enzyme prills are especially preferred for use herein. Such prills will generally range in size from about 100 to 1,000 microns, more preferably from about 200 to 800 microns and will be suspended throughout the non-aqueous liquid phase of the composition. Prills in the compositions of the present invention have been found, in comparison with other enzyme forms, to exhibit especially desirable enzyme stability in terms of retention of enzymatic activity over time. Thus, compositions which utilize enzyme prills need not contain conventional enzyme stabilizing such as must frequently be used when enzymes are incorporated into aqueous liquid detergents.

If employed, enzymes will normally be incorporated into the non-aqueous liquid compositions herein at levels sufficient to provide up to about 10 mg by weight, more typically from about 0.01 mg to about 5 mg, of active enzyme per gram of the composition. Stated otherwise, the non-aqueous liquid detergent compositions herein will typically comprise from about 0.001% to 5%, preferably from about 0.01% to 1% by weight, of a commercial enzyme preparation. Protease enzymes, for example, are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Optional Chelating Agents

The detergent compositions herein may also optionally contain a chelating agent which serves to chelate metal ions, e.g., iron and/or manganese, within the non-aqueous detergent compositions herein. Such chelating agents thus serve to form complexes with metal impurities in the composition which would otherwise tend to deactivate composition components such as the peroxygen bleaching agent. Useful chelating agents can include amino carboxylates, phosphonates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethyl-ethylenediaminetriacetates, nitrilotriacetates, ethylene-diamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, ethylenediaminedisuccinates and ethanol diglycines. The alkali metal salts of these materials are preferred.

Amino phosphonates are also suitable for use as chelating agents in the compositions of this invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylene-

phosphonates) as DEQUEST. Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Preferred chelating agents include hydroxy-ethyldiphosphonic acid (HEDP), diethylene triamine penta acetic acid (DTPA), ethylenediamine disuccinic acid (EDDS) and dipicolinic acid (DPA) and salts thereof. The chelating agent may, of course, also act as a detergent builder during use of the compositions herein for fabric laundering/bleaching. The chelating agent, if employed, can comprise from about 0.1% to 4% by weight of the compositions herein. More preferably, the chelating agent will comprise from about 0.2% to 2% by weight of the detergent compositions herein.

Optional Thickening, Viscosity Control and/or Dispersing Agents

The detergent compositions herein may also optionally contain a polymeric material which serves to enhance the ability of the composition to maintain its solid particulate components in suspension. Such materials may thus act as thickeners, viscosity control agents and/or dispersing agents. Such materials are frequently polymeric polycarboxylates but can include other polymeric materials such as polyvinylpyrrolidone (PVP) or polyamide resins.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight of the polymer.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 2,000 to 10,000, even more preferably from about 4,000 to 7,000, and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, Diehl, U.S. Patent 3,308,067, issued March 7, 1967. Such materials may also perform a builder function.

If utilized, the optional thickening, viscosity control and/or dispersing agents should be present in the compositions herein to the extent of from about 0.1% to 4% by weight. More preferably, such materials can comprise from about 0.5% to 2% by weight of the detergents compositions herein.

Optional Clay Soil Removal/Anti-redeposition Agents

The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and anti-redeposition properties. If used, soil materials can contain from about 0.01% to about 5% by weight of the compositions herein.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-anti-redeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/anti-redeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti-redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred anti-redeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Peroxygen Bleaching Agent With Optional Bleach Activators

Peroxygen bleaching agents may be organic or inorganic in nature. Inorganic peroxygen bleaching agents are frequently utilized in combination with a bleach activator.

Useful organic peroxygen bleaching agents include percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, Issued November 20, 1984; European Patent Application EP-A-133,354, Banks et al., Published February 20, 1985; and U.S. Patent 4,412,934, Chung et al., Issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacrylic acid (NAPAA) as described in U.S. Patent 4,634,551, Issued January 6, 1987 to Burns et al.

Inorganic peroxygen bleaching agents may also be used in the detergent compositions herein. Inorganic bleaching agents are in fact preferred. Such inorganic peroxygen compounds include alkali metal perborate and percarbonate materials, most preferably the percarbonates. For example, sodium perborate (e.g. mono- or tetrahydrate) can be used. Suitable inorganic bleaching agents can also include sodium or potassium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used. Frequently inorganic peroxygen bleaches will be coated with silicate, borate, sulfate or water-soluble surfactants. For example, coated percarbonate particles are available from various commercial sources such as FMC, Solvay Interox, Tokai Denka and Degussa.

Inorganic peroxygen bleaching agents, e.g., the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the in situ production in aqueous solution (i.e., during use of the compositions herein for fabric laundering/bleaching) of the peroxy acid corresponding to the bleach activator. Various non-limiting examples of activators are disclosed in U.S. Patent 4,915,854, Issued April 10, 1990 to Mao et al.; and U.S. Patent 4,412,934 Issued November 1, 1983 to Chung et al. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical. Mixtures thereof can also be used. See also the hereinbefore referenced U.S. 4,634,551 for other typical bleaches and activators useful herein.

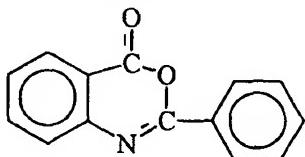
Other useful amido-derived bleach activators are those of the formulae:



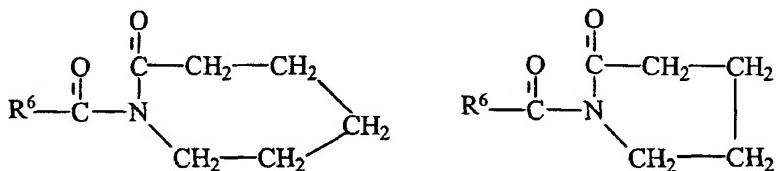
wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group, for example, oxybenzene sulfonate, -OOH, -OOM. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenol sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl) oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate and mixtures thereof as described in the hereinbefore referenced U.S. Patent 4,634,551. Such mixtures are characterized herein as (6-C₈-C₁₀ alkamido-caproyl)oxybenzenesulfonate.

Another class of useful bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al. in U.S. Patent 4,966, 723, Issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of useful bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R⁶ is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, Issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

If peroxygen bleaching agents are used, they will generally comprise from about 0.1% to 30% by weight of the composition. More preferably, peroxygen bleaching agent will comprise from about 1% to 20% by weight of the composition. Most preferably, peroxygen bleaching agent will be present to the extent of from about 5% to 20% by weight of the composition. If utilized, bleach activators can comprise from about 0.5% to 20%, more preferably from about 3% to 10%, by weight of the composition. Frequently, activators are employed such that the molar ratio of bleaching agent to activator ranges from about 1:1 to 10:1, more preferably from about 1.5:1 to 5:1.

In addition, it has been found that bleach activators, when agglomerated with certain acids such as citric acid, are more chemically stable.

Optional Bleach Catalysts

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S.

Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $Mn^{IV}2(u-O)_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(PF_6)_2$, $Mn^{III}2(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(ClO_4)_2$, $Mn^{IV}4(u-O)_6(1,4,7\text{-triazacyclononane})_4(ClO_4)_4$, $Mn^{III}Mn^{IV}4(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(ClO_4)_3$, $Mn^{IV}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})-(OCH_3)_3(PF_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

Cobalt bleach catalysts useful herein are known, and are described, for example, in M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[Co(NH_3)_5OAc]^-T_y^+$, wherein "OAc" represents an acetate moiety and " T_y^+ " is an anion, and especially cobalt pentaamine acetate chloride, $[Co(NH_3)_5OAc]Cl_2$; as well as $[Co(NH_3)_5OAc](OAc)_2$; $[Co(NH_3)_5OAc](PF_6)_2$; $[Co(NH_3)_5OAc](SO_4)_2$; $[Co(NH_3)_5OAc](BF_4)_2$; and $[Co(NH_3)_5OAc](NO_3)_2$ (herein "PAC").

These cobalt catalysts are readily prepared by known procedures, such as taught for example in the Tobe article and the references cited therein, in U.S. Patent 4,810,410, to Diakun et al, issued March 7, 1989, J. Chem. Ed. (1989), 66 (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952).

As a practical matter, and not by way of limitation, the compositions and cleaning processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in the aqueous washing medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm, and most preferably from about 0.1 ppm to about 5 ppm, of

the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic washing process, typical compositions herein will comprise from about 0.0005% to about 0.2%, more preferably from about 0.004% to about 0.08%, of bleach catalyst, especially manganese or cobalt catalysts, by weight of the cleaning compositions.

Optional Brighteners, Suds Suppressors, Dyes and/or Perfumes

The detergent compositions herein may also optionally contain conventional brighteners, suds suppressors, dyes and/or perfume materials. Such brighteners, suds suppressors, silicone oils, dyes and perfumes must, of course, be compatible and non-reactive with the other composition components in a non-aqueous environment. If present, brighteners suds suppressors, dyes and/or perfumes will typically comprise from about 0.0001% to 2% by weight of the compositions herein.

Polymeric Soil Release Agent

Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

Examples of polymeric soil release agents useful herein include U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink; U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.; European Patent Application 0 219 048, published April 22, 1987 by Kud, et al.; U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink; U.S. Patent 4,968,451, issued November 6, 1990 to J.J. Scheibel. Commercially available soil release agents include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany). Also see U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975. Examples of this polymer include the commercially available material ZELCON 5126 (from Dupont) and MILEASE T (from ICI). Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

Chelating Agents

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediamine-tetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-triacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Clay Soil Removal/Anti-redeposition Agents

The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Liquid detergent compositions typically contain about 0.01% to about 5% of these compositions.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Polymeric Dispersing Agents

Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid

form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

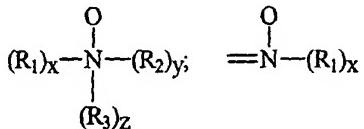
Dye Transfer Inhibiting Agents

The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the

composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: R-A_xP; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R₁, R₂, R₃ are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa <10, preferably pKa <7, more preferred pKa <6.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

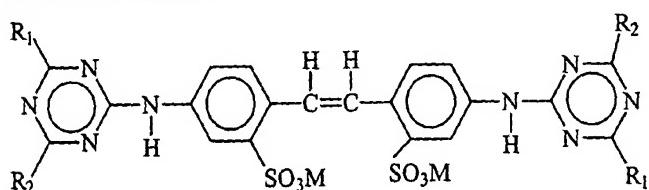
The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular

brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

COMPOSITION FORM

The aqueous based heavy-duty liquid detergent compositions disclosed herein can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those

containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and 11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

COMPOSITION PREPARATION AND USE

The aqueous based heavy-duty liquid detergent compositions of the present invention can be made by mixing and blending the desired ingredients with the desired solvent. In a typical process for preparing such compositions, essential and certain preferred optional components will be combined in a particular order and under certain conditions.

The compositions of this invention, prepared as hereinbefore described, can be used to form aqueous washing solutions for use in the laundering and bleaching of fabrics. Generally, an effective amount of such compositions is added to water, preferably in a conventional fabric laundering automatic washing machine, to form such aqueous laundering/bleaching solutions. The aqueous washing/bleaching solution so formed is then contacted, preferably under agitation, with the fabrics to be laundered and bleached therewith.

An effective amount of the liquid detergent compositions herein added to water to form aqueous laundering/bleaching solutions can comprise amounts sufficient to form from about 500 to 7,000 ppm of composition in aqueous solution. More preferably, from about 800 to 3,000 ppm of the detergent compositions herein will be provided in aqueous washing/bleaching solution.

The following examples illustrate the preparation and performance advantages of the modified alkyl benzene sulfonate surfactant mixtures containing aqueous liquid detergent compositions of the instant invention. Such examples, however, are not necessarily meant to limit or otherwise define the scope of the invention herein. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified. In the following Examples, the abbreviations for the various ingredients used for the compositions have the following meanings. In these Examples, the following abbreviation is used for a modified

alkylbenzene sulfonate, sodium salt form or potassium salt form, prepared according to any of the preceding process examples: MLAS

ABBREVIATIONS

LAS	Sodium linear alkyl benzene sulfonate
MBAS _x	Mid-chain branched primary alkyl (average total carbons = x) sulfate
MBAE _x S _z	Mid-chain branched primary alkyl (average total carbons = z) ethoxylate (average EO = x) sulfate, sodium salt
MBAE _x	Mid-chain branched primary alkyl (average total carbons = x) ethoxylate (average EO = 5)
Endolase	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
MEA	Monoethanolamine
PG	Propanediol
BPP	Butoxy - propoxy - propanol
EtOH	Ethanol
NaOH	Solution of sodium hydroxide
NaTS	Sodium toluene sulfonate
Citric acid	Anhydrous citric acid
CxyFA	C _{1x} -C _{1y} fatty acid
CxyEz	A C _{1x-1y} branched primary alcohol condensed with an average of z moles of ethylene oxide
Carbonate	Anhydrous sodium carbonate with a particle size between 200µm and 900µm
Citrate	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and 850 µm
TFAA	C16-18 alkyl N-methyl glucamide
LMFAA	C12-14 alkyl N-methyl glucamide
APA	C8-C10 amido propyl dimethyl amine
Fatty Acid (C12/14)	C12-C14 fatty acid
Fatty Acid (TPK)	Topped palm kernel fatty acid
Fatty Acid (RPS)	Rapeseed fatty acid
Borax	Na tetraborate decahydrate
PAA	Polyacrylic Acid (mw = 4500)
PEG	Polyethylene glycol (mw=4600)

MES	Alkyl methyl ester sulfonate
SAS	Secondary alkyl sulfate
NaPS	Sodium paraffin sulfonate
C45AS	Sodium C ₁₄ -C ₁₅ linear alkyl sulfate
CxyAS	Sodium C _{1x} -C _{1y} alkyl sulfate (or other salt if specified)
CxyEzS	Sodium C _{1x} -C _{1y} alkyl sulfate condensed with z moles of ethylene oxide (or other salt if specified)
CxyEz	A C _{1x-1y} branched primary alcohol condensed with an average of z moles of ethylene oxide
AQA	R ₂ N ⁺ (CH ₃) _x ((C ₂ H ₄ O) _y H) _z with R ₂ = C ₈ - C ₁₈ x+z = 3, x = 0 to 3, z = 0 to 3, y = 1 to 15.
STPP	Anhydrous sodium tripolyphosphate
Zeolite A	Hydrated Sodium Aluminosilicate of formula Na ₁₂ (Al ₁₀ SiO ₂) ₁₂ . 27H ₂ O having a primary particle size in the range from 0.1 to 10 micrometers
NaSKS-6	Crystalline layered silicate of formula δ-Na ₂ Si ₂ O ₅
Carbonate	Anhydrous sodium carbonate with a particle size between 200μm and 900μm
Bicarbonate	Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm
Silicate	Amorphous Sodium Silicate (SiO ₂ :Na ₂ O; 2.0 ratio)
Sulfate	Anhydrous sodium sulfate
PAE	ethoxylated (15-18) tetraethylene pentamine
PIE	ethoxylated polyethylene imine
PAEC	methyl quaternized ethoxylated dihexylene triamine
MA/AA	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
CMC	Sodium carboxymethyl cellulose
Protease	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
Cellulase	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
Amylase	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
Lipase	Lipolytic enzyme of activity 100kLU/g sold by NOVO

	Industries A/S under the tradename Lipolase
PB1	Anhydrous sodium perborate bleach of nominal formula NaBO ₂ .H ₂ O ₂
Percarbonate	Sodium Percarbonate of nominal formula 2Na ₂ CO ₃ .3H ₂ O ₂
NaDCC	Sodium dichloroisocyanurate
NOBS	Nonanoyloxybenzene sulfonate, sodium salt
TAED	Tetraacetyl ethylenediamine
DTPMP	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under Trade name Dequest 2060
	Photoactivated bleach Sulfonated Zinc Phthalocyanine bleach encapsulated in dextrin soluble polymer
Brightener 1	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
HEDP	1,1-hydroxyethane diphosphonic acid
SRP 1	Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
SRP 2	sulfonated ethoxylated terephthalate polymer
SRP 3	methyl capped ethoxylated terephthalate polymer
Silicone antifoam	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
Isofol 16	Condea trademark for C16 (average) Guerbet alcohols
CaCl ₂	Calcium chloride
MgCl ₂	Magnesium chloride
DTPA	Diethylene triamine pentaacetic acid

EXAMPLE 18

Liquid detergent compositions are made according to the following.

	A	B	C	D
C ₂₅ AE3S	2	8	7	5
MLAS	15	12	10	8
C ₁₂ -C ₁₄ alkyl dimethyl amine oxide	-	-	-	2
C ₂₅ AS	6	4	6	8

C ₂₄ N-methyl glucamide	5	4	3	3
C ₂₄ AES	6	1	1	1
C ₁₂ -C ₁₈ fatty acid	11	4	4	3
Citric acid	1	3	3	2
DTPMP	1	1	1	0.5
MEA	8	5	5	2
NaOH	1	2.5	1	1.5
PG	14.5	13.1	10.0	8
EtOH	1.8	4.7	5.4	1
Amylase (300KNU/g)	0.1	0.1	0.1	0.1
Lipase D96/L (100KNU/g)	0.15	0.15	0.15	0.15
Protease (35g/l)	0.5	0.5	0.5	0.5
Endolase	0.05	0.05	0.05	0.05
Cellulase	0.09	0.09	0.09	0.09
Terephthalate-based polymer	0.5	-	0.3	0.3
Boric acid	2.4	2.8	2.8	2.4
Sodium xylene sulfonate	-	3	-	-
2-butyl-octanol	1	1	1	1
Branched silicone	0.3	0.3	0.3	0.3
Water & minors	Up to 100%			

The above liquid detergent compositions (A-D) are found to be very efficient in the removal of a wide range of stains and soils from fabrics under various usage conditions.

EXAMPLE 19

The following compositions (E to J) are heavy duty liquid laundry detergent compositions according to the present invention.

Example #:	E	F	G	H	I	J
MLAS	17	15	7.0	7.0	12	12
C35AE3S/C25AE3S	2.0	9.0	-	-	7.0	7.0
C25 AE2.5S	-	-	12.0	12.0	-	-
C24 N-Me Glucamide	6.0	5.0	4.5	3.7	4.0	4.0
C35 E7	6.0	1.0	-	-	-	-
C23 E9	-	-	2.0	1.0	5.0	5.0
C10 APA	-	1.5	-	2.0	-	2.5
C24 Fatty Acid	7.5	1.1	2.0	4.0	5.0	5.0

C48 Fatty Acid	3.0	3.5	-	-	-	-
Citric Acid	1.0	3.5	3.0	3.0	3.0	3.0
Protease (34 g/#)	0.6	0.6	0.9	0.9	1.2	1.2
Lipase	0.1	0.1	0.1	0.1	0.2	0.2
Amylase (300KMU/g)	0.1	0.1	0.1	0.1	-	0.1
Cellulase	0.03	0.03	0.05	0.05	0.2	0.2
Endolase	0.1	0.1	-	-	-	-
Brightener 2	0.1	0.1	-	-	-	-
Boric Acid	3.0	3.0	3.5	3.5	4.0	4.0
MEA	8.0	4.0	1.0	1.5	7.0	7.0
NaOH	1.0	4.0	3.0	2.5	1.0	1.0
PG	12.0	12.0	7.5	7.5	7.0	7.0
EtOH	1.0	1.0	3.5	3.5	6.0	6.0
Na TS	-	-	2.5	2.5	-	-
Minors	Balance	Balance	Balance	Balance	Balance	Balance

The Following Examples illustrate aqueous based liquid detergent compositions according to the present invention.

EXAMPLE 20

Aqueous based heavy duty laundry detergent compositions F to J which comprise the mid-chain branched surfactants of the present invention are presented below.

Ingredient	F	G	H	I	J
MBAE1.8S14.4	10	12	14	16	20
MLAS	10	8	6	4	0
C23E9	2	2	2	2	2
LMFAA	5	5	5	5	0
Citric acid builder	3	3	3	3	5
Fatty acid builder	2	2	2	2	0
PAE	1	1	1.2	1.2	0.5
PG	8	8	8	8	4.5
EtOH	4	4	4	4	2
Boric acid	3.5	3.5	3.5	3.5	2
Sodium Cumene Sulfonate	3	3	3	3	0
pH =	8.0	8.0	8.0	8.0	7.0
Enzymes, dyes, water	balance	balance	balance	balance	balance

	100%	100%	100%	100%	100%
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EXAMPLE 21

The following aqueous liquid laundry detergent compositions K to O are prepared in accord with the invention:

	K	L	M	N	O
MLAS	1 - 7	7 - 12	12 - 17	17 - 22	1 - 35
Any combination of: C25 AExS*Na (x = 1.0 - 2.5) C25 AS (linear to high 2-alkyl) C14-17 NaPS C12-16 SAS C18 1,4 disulfate LAS C12-16 MES MBAE1.8S14.4 and / or MBAS14.4	15 - 21	10 - 15	5 - 10	0 - 5	0 - 25
LMFAA	0 - 3.5	0 - 3.5	0 - 3.5	0 - 3.5	0 - 8
C23E9 or C23E6.5	0 - 2	0 - 2	0 - 2	0 - 2	0 - 8
APA	0.5	0.5	0.5	0.5	0.5 - 2
Citric Acid	5	5	5	5	0 - 8
Fatty Acid (TPK or C12/14)	2	2	2	2	0 - 14
EtOH	4	4	4	4	0 - 8
PG	6	6	6	6	0 - 10
MEA	1	1	1	1	0 - 3
NaOH	3	3	3	3	0 - 7
Na TS	2.3	2.3	2.3	2.3	0 - 4
Na formate	0.1	0.1	0.1	0.1	0 - 1
Borax	2.5	2.5	2.5	2.5	0 - 5
Protease	0.9	0.9	0.9	0.9	0 - 1.3
Lipase	0.06	0.06	0.06	0.06	0 - 0.3
Amylase	0.15	0.15	0.15	0.15	0 - 0.4
Cellulase	0.05	0.05	0.05	0.05	0 - 0.2
PAE	0 - 0.6	0 - 0.6	0 - 0.6	0 - 0.6	0 - 2.5
PIE	1.2	1.2	1.2	1.2	0 - 2.5
PAEC	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4	0 - 2
SRP 2	0.2	0.2	0.2	0.2	0 - 0.5
Brightener 1 or 2	0.15	0.15	0.15	0.15	0 - 0.5
Silicone antifoam	0.12	0.12	0.12	0.12	0 - 0.3
Fumed Silica	0.0015	0.0015	0.0015	0.0015	0-0.003
Perfume	0.3	0.3	0.3	0.3	0 - 0.6
Dye	0.0013	0.0013	0.0013	0.0013	0-0.003

Moisture/minors	Balance	Balance	Balance	Balance	Balance
Product pH (10% in DI water)	7.7	7.7	7.7	7.7	6 - 9.5

EXAMPLE 22

The following aqueous liquid laundry detergent compositions P to T are prepared in accord with the invention:

	P	Q	R	S	T
MLAS	2	6.25	10.5	14.75	19
Any combination of: C25E1-3S C25 AS C14-17 NaPS C12-16 SAS C18 1,4 disulfate LAS C12-16 MES MBAE1S14.4 and / or MBAS14.4	17	12.75	8.5	4.25	0
LMFAA	1 - 5.5	1 - 5.5	1 - 5.5	1 - 5.5	1 - 5.5
C23E9	4 - 6	4 - 6	4 - 6	4 - 6	4 - 6
APA	0 - 1.5	0 - 1.5	0 - 1.5	0 - 1.5	0 - 1.5
Citric Acid	1	1	1	1	1
Fatty Acid (TPK,C12/14)	7.5	7.5	7.5	7.5	7.5
Fatty Acid (RPS)	3.1	3.1	3.1	3.1	3.1
EtOH	0-6	0-6	0-6	0-6	0-6
PG	4-10	4-10	4-10	4-10	4-10
MEA	3-8	3-8	3-8	3-8	3-8
NaOH	1.5	1.5	1.5	1.5	1.5
Na TS	0 - 2	0 - 2	0 - 2	0 - 2	0 - 2
Borax	2 - 2.5	2 - 2.5	2 - 2.5	2 - 2.5	2 - 2.5
CaCl2	0.02	0.02	0.02	0.02	0.02
Protease	0.3 - 1	0.3 - 1	0.3 - 1	0.3 - 1	0.3 - 1
Lipase	0.05 - 0.3	0.05 - 0.3	0.05 - 0.3	0.05 - 0.3	0.05 - 0.3
Amylase	0.05 - 0.5	0.05 - 0.5	0.05 - 0.5	0.05 - 0.5	0.05 - 0.5
Cellulase	0.3	0.3	0.3	0.3	0.3
PIE	1.2	1.2	1.2	1.2	0 - 2.5
PAEC	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4	0 - 2
PAE	0.2 - 0.7	0.2 - 0.7	0.2 - 0.7	0.2 - 0.7	0.2 - 0.7
SRP 3	0.1 - 0.2	0.1 - 0.2	0.1 - 0.2	0.1 - 0.2	0.1 - 0.2
Brightener 1 or 2	0.15	0.15	0.15	0.15	0.15
Silicone antifoam	0.2 - 0.25	0.2 - 0.25	0.2 - 0.25	0.2 - 0.25	0.2 - 0.25
Isofol 16	0 - 2	0 - 2	0 - 2	0 - 2	0 - 2
Perfume	0.5	0.5	0.5	0.5	0.5
Moisture/minors	Balance	Balance	Balance	Balance	Balance
pH (10% in DI water)	7.6	7.6	7.6	7.6	7.6

EXAMPLE 23

Aqueous based heavy duty liquid laundry detergent compositions which comprise the mid-chain branched surfactants of the present invention are presented below.

Ingredient	A	B	C	D	E
MLAS	10	12	14	16	20
Na C25AES surfactant	10	8	6	4	0
C23EO9 surfactant	2	2	2	2	2
C12alkyl glucose amide	5	5	5	5	0
Citric acid builder	3	3	3	3	5
Fatty acid builder	2	2	2	2	0
Tetraethylenepentamine ethoxylated (15-18)	1	1	1.2	1.2	0.5
Propanediol	8	8	8	8	4.5
Ethanol	4	4	4	4	2
Boric acid	3.5	3.5	3.5	3.5	2
Sodium Cumene Sulfonate	3	3	3	3	0
pH =	8.0	8.0	8.0	8.0	7.0
Enzymes, dyes, water	balance	balance	balance	balance	balance
	100%	100%	100%	100%	100%

Additional Synthesis ExamplesEXAMPLE 24

Linear and Branched Alkylbenzene Mixture

With a 2/3-Phenyl Index of about 200 and a 2-Methyl-2-Phenyl Index of about 0.02

(alkylbenzene mixture according to the invention)

110.25 g of the substantially mono methyl branched olefin mixture of example 2, 36.75 g of a nonbranched olefin mixture (decene : undecene : dodecene : tridecene ratio of 2 : 9 : 20 : 18) and 36 g of a shape selective zeolite catalyst (acidic beta zeolite catalyst; Zeocal™ PB/H) are added to a 2 gallon stainless steel, stirred autoclave. Residual olefin and catalyst in the container are washed into the autoclave with 300 mL of n-hexane and the autoclave is sealed. From outside the autoclave cell, 2000 g of benzene (contained in a isolated vessel and added by way of an isolated pumping system inside the isolated autoclave cell) is added to the autoclave. The autoclave is purged twice with 250 psig N₂, and then charged to 60 psig N₂. The mixture is stirred and heated to about 200°C for about 4-5 hours. The autoclave is cooled to about 20°C overnight. The valve is opened leading from the autoclave to the benzene condenser and collection tank. The

autoclave is heated to about 120°C with continuous collection of benzene. No more benzene is collected by the time the reactor reaches 120°C. The reactor is then cooled to 40°C and 750 g of n-hexane is pumped into the autoclave with mixing. The autoclave is then drained to remove the reaction mixture. The reaction mixture is filtered to remove catalyst and the n-hexane is removed under vacuum. The product is distilled under vacuum (1-5 mm of Hg). A modified alkylbenzene mixture with a 2/3-Phenyl index of about 200 and a 2-methyl-2-phenyl index of about 0.02 is collected from 76°C - 130°C (167 g).

EXAMPLE 25

Modified Alkylbenzenesulfonic Acid Mixture according to the invention

(Branched and Nonbranched Alkylbenzenesulfonic Acid Mixture)

with a 2/3-Phenyl Index of about 200 and a 2-Methyl-2-Phenyl Index of about 0.02
The modified alkylbenzene mixture of example 24 is sulfonated with a molar equivalent of chlorosulfonic acid using methylene chloride as solvent. The methylene chloride is removed to give 210 g of a modified alkylbenzenesulfonic acid mixture with a 2/3-Phenyl index of about 200 and a 2-methyl-2-phenyl index of about 0.02.

EXAMPLE 26

Modified Alkylbenzenesulfonate, Sodium Salt Mixture According to the invention

(Branched and Nonbranched Alkylbenzenesulfonate, Sodium Salt Mixture)

with a 2/3-Phenyl Index of about 200 and a 2-Methyl-2-Phenyl Index of about 0.02
The modified alkylbenzenesulfonic acid of example 25 is neutralized with a molar equivalent of sodium methoxide in methanol and the methanol is evaporated to give 225 g of a modified alkylbenzenesulfonate, sodium salt mixture with a 2/3-Phenyl index of about 200 and a 2-methyl-2-phenyl index of about 0.02.

EXAMPLE 27

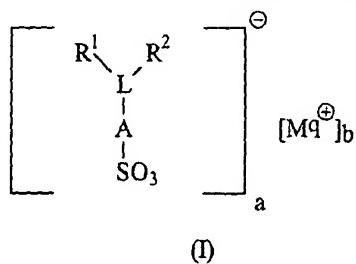
Detergent compositions as in Examples 18-23 are repeated, substituting MLAS with the product of Example 25.

What is claimed is:

1. An aqueous based heavy-duty liquid detergent composition comprising:

(i) from 5% to 70% by weight of composition of a modified alkylbenzene sulfonate surfactant mixture comprising:

(a) from 15% to 99% by weight of surfactant mixture, a mixture of branched alkylbenzene sulfonates having formula (I):

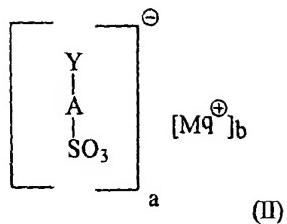


wherein L is an acyclic aliphatic moiety consisting of carbon and hydrogen, said L having two methyl termini and said L having no substituents other than A, R¹ and R²; and wherein said mixture of branched alkylbenzene sulfonates contains two or more of said branched alkylbenzene sulfonates differing in molecular weight of the anion of said formula (I) and wherein said mixture of branched alkylbenzene sulfonates has

- a sum of carbon atoms in R¹, L and R² of from 9 to 15;
- an average aliphatic carbon content of from 10.0 to 14.0 carbon atoms;

M is a cation or cation mixture having a valence q; a and b are integers selected such that said branched alkylbenzene sulfonates are electroneutral; R¹ is C₁-C₃ alkyl; R² is selected from H and C₁-C₃ alkyl; A is a benzene moiety; and

(b) from 1% to 85% by weight of surfactant mixture, of a mixture of nonbranched alkylbenzene sulfonates having formula (II):



wherein a, b, M, A and q are as defined hereinbefore and Y is an unsubstituted linear aliphatic moiety consisting of carbon and hydrogen having two methyl termini, and wherein said Y has a sum of carbon atoms of from 9 to 15, preferably from 10 to 14, and said Y has an average aliphatic carbon content of from 10.0 to 14.0; and

wherein said modified alkylbenzene sulfonate surfactant mixture is further characterized by a 2/3-phenyl index of from 160 to 275;

(ii) from 0.1 to 8% of a co-surfactant composition selected from the group consisting of alkyl polyhydroxy fatty acid amide, alkyl amidopropyl dimethyl amine and mixtures thereof; and

(iii) from 30% to 95%, of an aqueous liquid carrier;

wherein said composition is further characterized by a 2/3-phenyl index of from 160 to 275.

2. The detergent composition according to Claim 1 wherein said M is selected from H, Na, K and mixtures thereof, said a=1, said b=1, said q=1, and said modified alkylbenzene sulfonate surfactant mixture has a 2-methyl-2-phenyl index of less than 0.3.

3. The detergent composition according to Claim 2 wherein said 2-methyl-2-phenyl index is from 0 to 0.1.

4. The detergent composition according to Claim 3 wherein said modified alkylbenzene sulfonate surfactant mixture is the product of a process using as catalyst a zeolite beta.

5. The detergent composition according to Claim 4 wherein said catalyst is in at least partially acidic form.

6. The detergent composition according to Claim 2 consisting essentially of said mixture of branched alkylbenzene sulfonates and nonbranched alkylbenzene sulfonates, wherein said 2-methyl-2-phenyl index of said modified alkylbenzene sulfonate surfactant mixture is less than 0.1, and wherein in said mixture of branched and nonbranched alkylbenzene sulfonates, said average aliphatic carbon content is from 11.0 to 12.0 carbon atoms; said R¹ is methyl; said R² is selected from H and methyl provided that in at least 0.7 mole fraction of said branched alkylbenzene sulfonates R² is H; and wherein said sum of carbon atoms in R¹, L and R² is from 10 to 14; and further wherein in said mixture of nonbranched alkylbenzene sulfonates, said Y has a sum of carbon atoms of from 10 to 14 carbon atoms, said average aliphatic carbon content of said nonbranched alkylbenzene sulfonates is from 11.0 to 12.0 carbon atoms, and said M is a monovalent cation or cation mixture selected from H, Na and mixtures thereof.

7. An aqueous based heavy-duty liquid detergent composition comprising:

- (i) a modified alkylbenzene sulfonate surfactant mixture comprising the product of a process comprising the steps of:
 - (I) alkylating benzene with an alkylating mixture in the presence of a zeolite beta catalyst;
 - (II) sulfonating the product of (I); and
 - (III) neutralizing the product of (II);wherein said alkylating mixture comprises:
 - (a) from 1% to 99.9%, by weight of alkylating mixture of branched C₉-C₂₀ monoolefins, said branched monoolefins having structures identical with those of the branched monoolefins formed by dehydrogenating branched paraffins of formula R¹LR² wherein L is an acyclic aliphatic moiety consisting of carbon and hydrogen and containing two terminal methyls; R¹ is C₁ to C₃ alkyl; and R² is selected from H and C₁ to C₃ alkyl; and
 - (b) from 0.1% to 85%, by weight of alkylating mixture of C₉-C₂₀ linear aliphatic olefins;

wherein said alkylating mixture contains said branched C₉-C₂₀ monoolefins having at least two different carbon numbers in said C₉-C₂₀ range, and has a mean carbon content of from 9.0 to 15.0 carbon atoms; and wherein said components (a) and (b) are at a weight ratio of at least 15:85;

(ii) from 0.1 to 8% of a co-surfactant composition selected from the group consisting of alkyl polyhydroxy fatty acid amide, alkyl amidopropyl dimethyl amine and mixtures thereof; and

(iii) from 30% to 95%, of an aqueous liquid carrier;

wherein said composition is further characterized by a 2/3-phenyl index of from 160 to 275.

8. An aqueous based heavy-duty liquid detergent composition comprising:

(i) a modified alkylbenzene sulfonate surfactant mixture consisting essentially of the product of a process comprising the steps, in sequence, of:

- (I) alkylating benzene with an alkylating mixture in the presence of a zeolite beta catalyst;
- (II) sulfonating the product of (I); and
- (III) neutralizing the product of (II);

wherein said alkylating mixture comprises:

(a) from 1% to 99.9%, by weight of alkylating mixture of a branched alkylating agent selected from the group consisting of:

- (A) C₉-C₂₀ internal monoolefins R¹LR² wherein L is an acyclic olefinic moiety consisting of carbon and hydrogen and containing two terminal methyls;
- (B) C₉-C₂₀ alpha monoolefins R¹AR² wherein A is an acyclic alpha-olefinic moiety consisting of carbon and hydrogen and containing one terminal methyl and one terminal olefinic methylene;
- (C) C₉-C₂₀ vinylidene monoolefins R¹BR² wherein B is an acyclic vinylidene olefin moiety consisting of carbon and hydrogen

and containing two terminal methyls and one internal olefinic methylene;

(D) C₉-C₂₀ primary alcohols R¹QR² wherein Q is an acyclic aliphatic primary terminal alcohol moiety consisting of carbon, hydrogen and oxygen and containing one terminal methyl;

(E) C₉-C₂₀ primary alcohols R¹ZR² wherein Z is an acyclic aliphatic primary nonterminal alcohol moiety consisting of carbon, hydrogen and oxygen and containing two terminal methyls; and

(F) mixtures thereof;

wherein in any of (A)-(F), said R¹ is C₁ to C₃ alkyl and said R² is selected from H and C₁ to C₃ alkyl; and

(b) from 0.1% to 85%, by weight of alkylating mixture of C₉-C₂₀ linear alkylating agent selected from C₉-C₂₀ linear aliphatic olefins, C₉-C₂₀ linear aliphatic alcohols and mixtures thereof;

wherein said alkylating mixture contains said branched alkylating agents having at least two different carbon numbers in said C₉-C₂₀ range, and has a mean carbon content of from 9.0 to 15.0 carbon atoms; and wherein said components (a) and (b) are at a weight ratio of at least 15:85;

(ii) from 0.1 to 8% of a co-surfactant composition selected from the group consisting of alkyl polyhydroxy fatty acid amide, alkyl amidopropyl dimethyl amine and mixtures thereof; and

(iii) from 30% to 95%, of an aqueous liquid carrier;

wherein said composition is further characterized by a 2/3-phenyl index of from 160 to 275.

9. The detergent composition according to Claim 8 wherein said alkylating mixture consists essentially of:

(a) from 0.5% to 47.5%, by weight of alkylating mixture of said branched alkylating agent selected from:

(G) C₉-C₁₄ internal monoolefins R¹LR² wherein L is an acyclic olefinic moiety consisting of carbon and hydrogen and containing two terminal methyls;

(H) C₉-C₁₄ alpha monoolefins R¹AR² wherein A is an acyclic alpha-olefinic moiety consisting of carbon and hydrogen and containing one terminal methyl and one terminal olefinic methylene; and

(J) mixtures thereof;

wherein in any of (G), (H) and (J), said R¹ is methyl, and said R² is H or methyl provided that in at least 0.7 mole fraction of the total of said monoolefins, R² is H; and

(b) from 0.1% to 25%, by weight of alkylating mixture of C₉-C₁₄ linear aliphatic olefins; and

(c) from 50% to 98.9%, by weight of alkylating mixture of carrier materials selected from paraffins and inert nonparaffinic solvents;

wherein said alkylating mixture contains said branched alkylating agents having at least two different carbon numbers in said C₉-C₁₄ range, and has a mean carbon content of from 11.0 to 12.0 carbon atoms; and wherein said components (a) and (b) are at a weight ratio of from 51:49 to 90:10.

10. The detergent composition according to Claim 9 wherein in step (II) comprises removal of components other than monoalkylbenzene prior to contacting the product of step (I) with sulfonating agent.

11. The detergent composition according to Claim 9 wherein a hydrotrope, hydrotrope precursor, or mixtures thereof is added after step (I).

12. The detergent composition according to Claim 9 wherein a hydrotrope, hydrotrope precursor or mixtures thereof is added during or after step (II) and prior to step (III).

13. The detergent composition according to Claim 9 wherein a hydrotrope is added during or after step (III).

14. The detergent composition according to Claim 9 wherein said acidic zeolite beta catalyst is an HF-treated calcined zeolite beta catalyst.

15. The detergent composition according to Claim 9 wherein in step (I) said alkylation is performed at a temperature of from 125°C to 230°C and at a pressure of from 50 psig to 1000 psig.

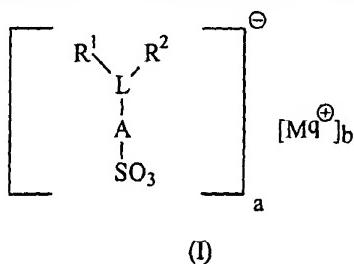
16. The detergent composition according to Claim 9 wherein in step (I) said alkylation is performed at a temperature of from 175°C to 215°C, at a pressure of from 100 psig to 250 psig, and a time of from 0.01 hour to 18 hours.

17. The detergent composition according to Claim 9 wherein step (II) is performed using a sulfonating agent selected from the group consisting of sulfur trioxide, sulfur trioxide/air mixtures, and sulfuric acid.

18. An aqueous based heavy-duty liquid detergent composition comprising:

(i) from 5% to 70% by weight of composition of a modified alkylbenzene sulfonate surfactant mixture comprising:

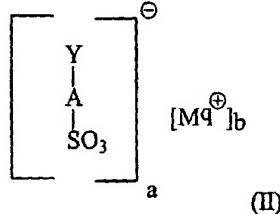
(a) from 15% to 99% by weight of surfactant mixture, a mixture of branched alkylbenzene sulfonates having formula (I):



wherein L is an acyclic aliphatic moiety consisting of carbon and hydrogen, said L having two methyl termini and said L having no substituents other than A, R¹ and R²; and wherein said mixture of branched alkylbenzene sulfonates contains two or more of said branched

alkylbenzene sulfonates differing in molecular weight of the anion of said formula (I) and wherein said mixture of branched alkylbenzene sulfonates has

- a sum of carbon atoms in R¹, L and R² of from 9 to 15;
- an average aliphatic carbon content of from 10.0 to 14.0 carbon atoms; M is a cation or cation mixture having a valence q; a and b are integers selected such that said branched alkylbenzene sulfonates are electroneutral; R¹ is C₁-C₃ alkyl; R² is selected from H and C₁-C₃ alkyl; A is a benzene moiety; and
- (b) from 1% to 85% by weight of surfactant mixture, of a mixture of nonbranched alkylbenzene sulfonates having formula (II):



wherein a, b, M, A and q are as defined hereinbefore and Y is an unsubstituted linear aliphatic moiety consisting of carbon and hydrogen having two methyl termini, and wherein said Y has a sum of carbon atoms of from 9 to 15, preferably from 10 to 14, and said Y has an average aliphatic carbon content of from 10.0 to 14.0; and

wherein said modified alkylbenzene sulfonate surfactant mixture is further characterized by a 2/3-phenyl index of from 160 to 275 and wherein said modified alkylbenzene sulfonate surfactant mixture has a 2-methyl-2-phenyl index of less than 0.3;

- (ii) from 0.1 to 8% of a co-surfactant composition selected from the group consisting of alkyl polyhydroxy fatty acid amide, alkyl amidopropyl dimethyl amine and mixtures thereof;
- (iii) from 0.00001% to 99.9% of composition of a surfactant selected from the group consisting of anionic surfactants other than those of (i), nonionic

surfactants, zwitterionic surfactants, cationic surfactants, amphoteric surfactant and mixtures thereof; and

(iv) from 30% to 95%, of an aqueous liquid carrier;

provided that when said detergent composition comprises any alkylbenzene sulfonate surfactant other than said modified alkylbenzene sulfonate surfactant mixture, said detergent composition is further characterized by an overall 2/3-phenyl index of at least 160, wherein said overall 2/3-phenyl index is determined by measuring 2/3-phenyl index, as defined herein, on a blend of said modified alkylbenzene sulfonate surfactant mixture and said any other alkylbenzene sulfonate to be added to said detergent composition, said blend, for purposes of measurement, being prepared from aliquots of said modified alkylbenzene sulfonate surfactant mixture and said other alkylbenzene sulfonate not yet exposed to any other of said components of the detergent composition; and further provided that when said detergent composition comprises any alkylbenzene sulfonate surfactant other than said modified alkylbenzene sulfonate surfactant mixture, said detergent composition is further characterized by an overall 2-methyl-2-phenyl index of less than 0.3, wherein said overall 2-methyl-2-phenyl index is to be determined by measuring 2-methyl-2-phenyl index, as defined herein, on a blend of said modified alkylbenzene sulfonate surfactant mixture and any other alkylbenzene sulfonate to be added to said detergent composition, said blend, for purposes of measurement, being prepared from aliquots of said modified alkylbenzene sulfonate surfactant mixture and said other alkylbenzene sulfonate not yet exposed to any other of said components of the detergent composition.

19. The detergent composition according to Claim 18 which is substantially free from alkylbenzene sulfonate surfactants other than said modified alkylbenzene sulfonate surfactant mixture.

20. The detergent composition according to Claim 18 which comprises, in said component (iii), at least 0.1%, of a commercial C₁₀-C₁₄ linear alkylbenzene sulfonate surfactant having a 2/3 phenyl index of from 75 to 160.

21. The detergent composition according to Claim 18 which comprises, in said component (iii), at least 0.1% of a commercial highly branched alkylbenzene sulfonate surfactant.
22. The detergent composition according to Claim 18 which comprises, in said component (iii), a nonionic surfactant at a level of from 0.5% to 25% by weight of said detergent composition, and wherein said nonionic surfactant is a polyalkoxylated alcohol in capped or non-capped form having:
 - a hydrophobic group selected from linear C₁₀-C₁₆ alkyl, mid-chain C₁-C₃ branched C₁₀-C₁₆ alkyl, guerbet branched C₁₀-C₁₆ alkyl, and mixtures thereof; and
 - a hydrophilic group selected from 1-15 ethoxylates, 1-15 propoxylates 1-15 butoxylates and mixtures thereof, in capped or uncapped form.
23. The detergent composition according to Claim 18 which comprises, in said component (iii), an alkyl sulfate surfactant at a level of from 0.5% to 25% by weight of said detergent composition, wherein said alkyl sulfate surfactant has a hydrophobic group selected from linear C₁₀-C₁₈ alkyl, mid-chain C₁-C₃ branched C₁₀-C₁₈ alkyl, guerbet branched C₁₀-C₁₈ alkyl, and mixtures thereof and a cation selected from Na, K and mixtures thereof.
24. The detergent composition according to Claim 18 which comprises, in said component (iii), an alkyl(polyalkoxy)sulfate surfactant at a level of from 0.5% to 25% by weight of said detergent composition, wherein said alkyl(polyalkoxy)sulfate surfactant has
 - a hydrophobic group selected from linear C₁₀-C₁₆ alkyl, mid-chain C₁-C₃ branched C₁₀-C₁₆ alkyl, guerbet branched C₁₀-C₁₆ alkyl, and mixtures thereof; and
 - a (polyalkoxy)sulfate hydrophilic group selected from 1-15 polyethoxysulfate, 1-15 polypropoxysulfate, 1-15 polybutoxysulfate, 1-15 mixed poly(ethoxy/propoxy/butoxy)sulfates, and mixtures thereof, in capped or uncapped form; and
 - a cation selected from Na, K and mixtures thereof.

25. The detergent composition according to any one of Claims 1 to 24, further comprising conventional detergent additives selected from the group consisting of builders, bleaching compounds, polymeric dispersing agents, anti-redeposition agents polymeric soil release agents, enzymes, additional co-surfactants and mixture thereof.
26. The detergent composition according to any one of Claims 1 to 25, further comprises 6-nonylamino-6-oxoperoxyacrylic acid.
27. The detergent composition according to any one of Claims 1 to 26, further comprising a bleach activator, wherein said bleach activator is selected from the group consisting of (6-octanamido-caproyl) oxybenzenesulfonate, (6-nonanamidocaproyl) oxybenzenesulfonate, (6-decanamido-caproyl) oxybenzenesulfonate and mixtures thereof.
28. The detergent composition according to Claim 1 wherein said modified alkylbenzene sulfonate surfactant mixture is prepared by a process comprising a step selected from:
blending a mixture of branched and linear alkylbenzene sulfonate surfactants having a 2/3-phenyl index of 500 to 700 with an alkylbenzene sulfonate surfactant mixture having a 2/3-phenyl index of 75 to 160; and
blending a mixture of branched and linear alkylbenzenes having a 2/3-phenyl index of 500 to 700 with an alkylbenzene mixture having a 2/3-phenyl index of 75 to 160 and sulfonating said blend.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/29947

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 00 12451 A (PROCTER & GAMBLE) 9 March 2000 (2000-03-09) page 26, paragraph 3 examples 4,8 ---	1-10, 14-20, 22-25,28
P,X	WO 99 07656 A (PROCTER & GAMBLE) 18 February 1999 (1999-02-18) page 19, paragraph 4 page 22, paragraph 4 -page 23, paragraph 1 page 34, paragraph 3 -page 45, paragraph 4 examples 1-5,8 claims 1-21 ---	1-3,6, 18-20, 22-25,28 4,5, 7-10, 14-17
A		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

	International Application No PCT/US 99/29947
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
P, X	WO 99 05244 A (PROCTER & GAMBLE) 4 February 1999 (1999-02-04)	1-3, 6, 18, 19, 22-25, 28
A	page 8, paragraph 6 -page 19, paragraph 2 example 11 claims 1-9 ---	7-10, 15, 17
A	EP 0 615 968 A (UOP INC) 21 September 1994 (1994-09-21) page 6, line 12 -page 7, line 39 claim 6 ---	1-10, 14, 15, 17, 28
A	US 4 301 316 A (YOUNG LEWIS B) 17 November 1981 (1981-11-17) cited in the application abstract column 3, line 21 -column 4, line 25 example 2 claims 1-5, 7, 10, 11 -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/29947

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